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RAPID TESTING OF FRESH CONCRETE

Paul A. Howdyshell

Army Construction Engineering Research Laboratory
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This Conference Proceedings contains papers presented at the May 1975 Rapid Testing of Fresh Concrete Conference sponsored by the U.S. Army Corps of Engineers, Construction Engineering Research Laboratory (CERL). The papers contain state of the art information about techniques to determine water and cement content of fresh concrete, including chemical-mechanical and nuclear methods.

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FOREWORD

The need for more rapid techniques to evaluate concrete quality has long been recognized. Recent concerted efforts have resulted in the development of rapid (less than 15 min) field methods for determining the water and/or cement contents of fresh concrete. Several of these test methods are ready for general field use; however, the potential users are not aware of the current state-of-the-art. Recognizing this situation, the Materials Systems and Science Division (MS) of the Construction Engineering Research Laboratory (CERL), Champaign, IL, initiated plans for a conference to acquaint potential users with recent developments in field techniques by means of formal presentations and equipment demonstrations.

The papers contained in these proceedings are arranged in order of their presentations at the conference. The first session presented papers about chemical-mechanical techniques to determine water and cement content, as well as data relating water and cement content test results to concrete strength potential. The second session presented papers about nuclear techniques to determine water and cement contents of fresh concrete.

CERL personnel actively engaged in the conference development, planning, and conduct were: Mr. P. A. Howdyshell, Construction Materials Branch (MSC); Dr. G. R. Williamson, Chief, MSC; Ms. C. Bennett, MSC; and Mr. R. Muncy, MS Testing Branch.

Appreciation is extended to the speakers who not only took the time to prepare and present papers, but also assisted with the equipment demonstrations. Assistance with the editing and preparation of the proceedings provided by the CERL Technical Information Branch is appreciated.

Mr. J. J. Healy is Chief of MS, COL M. D. Remus is Commander and Director of CERL, and Dr. L. R. Shaffer is Deputy Director.

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DETERMINATION OF THE COMPOSITION OF FRESH CONCRETE BY NONNUCLEAR MEANS

by

Sandor Popovics

Professor
Northern Arizona University
Flagstaff, Arizona

Presented at CERL Conference on
RAPID TESTING OF FRESH CONCRETE
Champaign, Illinois
May 1975

ABSTRACT

Quite a few methods have been recommended in the technical literature for the determination of the cement and water contents as well as the water/cement ratio of a fresh concrete. This not only shows the importance of the problem but the fact that none of the existing methods is completely satisfactory for engineers.

This paper discusses several of the published methods for determination of cement content, including the well-known Dunagan method and some of its variants, another mechanical method based on consistency measurements by two different techniques, and two physicochemical methods.

Although drying is simplest method for determining water content it is not accurate enough. Other methods of estimating the water content include calculating the weight of the solids in the concrete, using chemical means; measuring the electrical resistance or capacitance, or the thermal conductivity or the microwave absorption; and performing repeated consistency tests. The methods suggested for determination of the water/cement ratio are measuring essentially the water content.

Further research concerning the analysis of the composition of fresh concrete is clearly indicated.

DETERMINATION OF THE COMPOSITION OF FRESH CONCRETE BY NONNUCLEAR MEANS

by

Sandor Popovics

INTRODUCTION

With the increasing speed of construction, the larger volumes of concrete that are now placed at one time, and the emphasis on quality control, the need for factual evidence of the suitability of the concrete at the earliest possible stage in the production cycle becomes increasingly important. The use of a convenient method of analyzing the fresh concrete can not only confirm compliance with the specified composition of the mixture but also enable early corrective action.

The three usual reasons for analyzing the composition of a concrete are:

1. To see to what extent the composition complies with the specifications

2. To check within-batch or between-batch uniformity of a concrete

3. To estimate the strength potential of the concrete.

To meet any of these goals, it is considered that the ideal method of analyzing fresh concrete should comply with the following requirements:[1,2]

1. It should provide the cement and water contents with an accuracy of, say, 1 percent and with an adequate reproducibility

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[1] Kenny, R. A. and Tulloch, B.M.L.G., "Analyzing Fresh Concrete," *Concrete*, Vol 6, No. 3 (March 1972), pp 23-27.

[2] Forrester, J. A., "Review of Techniques for the Rapid Analysis of Fresh Concrete," *Departmental Note*, DN/4008 (Cement and Concrete Association, London, October 1968).

2. No prior detailed knowledge of the properties of the aggregate or cement should be required

3. It should be suitable for use with a wide range of different types of aggregate and cement

4. It should be capable of being carried out rapidly, preferably within 10 minutes

5. It should be operable by trained but not necessarily highly qualified personnel

6. It should be suitable for use in the field and acceptable to engineers

7. It would be desirable for the separated mixture-constituents to be available for inspection

8. It should use robust apparatus capable of automation

9. It should be relatively cheap in terms of manpower, apparatus and materials requirements.

The importance determining the composition of fresh concrete is indicated by the fact that numerous principles have been suggested and quite a few test methods have been developed for this purpose. Unfortunately, none of them comply with all the requirements listed above. Therefore, further effort to find a more practical method for the analysis of fresh concrete is clearly justified.

Some of the principles and methods available in the literature are discussed below. For all these methods two points should be kept in mind: (1) the sampling of fresh concrete should be performed very carefully and (2) the test has to be commenced virtually as soon as the concrete has been discharged from the mixer because loss of water can occur even if evaporation is prevented, for instance by the hydration of the cement.[3]

DETERMINATION OF THE CEMENT CONTENT

The first method for determining the cement content in the fresh

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[3] Neville, A. M., "Analysis of Fresh Concrete," *Concrete*, Vol 7, No. 3 (March 1973) p 37.

concrete was offered probably by Griesenauer[4] and then by Dunagan.[5,6] Briefly, this method consists of weighing an 8- to 10-lb (4 to 5 kg) sample of concrete in air; weighing it under water, with which it is diluted; and wet-screening it through the No. 4 (4.75 mm) and No. 100 (0.15 mm) sieves. Computations involve the specific gravity of the materials, the amount of aggregate retained on the No. 4 and No. 100 sieves, and the amount of cement passing the No. 100 sieve. Corrections may be made for absorption of aggregate and for overlapping particle sizes (such as cement and silt) as determined by separate tests on materials used in the concrete.

This method has been used quite extensively[7,8,9,10,11] and the principle of wet screening for determination of the cement content has been accepted in several standards.[12,13,14] This writer's experience with the Dunagan method has been favorable as long as the aggregate came from the same source, the same skilled technician performed the test, and the length of testing time was not a problem. Others have

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[4] Griesenauer, G. J., "A Substitute for the Compression Test of Concrete: A Method for Determining the Composition and Quality of Concrete While in Its Plastic State," *Engineering News-Record*, Vol 103, No. 22 (1929), p 846.

[5] Dunagan, W. M., "Proposed Method of Test for the Field Determination of the Constituents of Fresh Concrete," *Proceedings*, ASTM, Vol 31, Part I (1931), pp 383-385.

[6] Dunagan, W. M., "Method of Determining the Constituents of Fresh Concrete," *Proceedings*, ACI, Vol 26 (1930), pp 202-210.

[7] Nettles, H. R., and Holme, J. M., "A Study of the Analysis of Fresh Concrete with the Dunagan Buoyancy Apparatus," *Proceedings*, ASTM, Vol 33, Part I (1933), pp 297-307.

[8] Blanchette, W. A., "Washing Machine Designed for Use in Determining Constituents of Fresh Concrete," *Public Roads*, Vol 13, No. 9 (1932), p 151.

[9] Cook, G. C., "Effect of Time of Haul on Strength and Consistency of Ready-Mixed Concrete," *ACI Journal*, Proc. Vol 39 (1952) pp 413-428.

[10] Hollister, S. C., "Tests of Concrete from a Transit Mixer," *Proceedings*, ACI, Vol 28 (1952), pp 405-417.

[11] Slater, W. A., "Tests of Concrete Conveyed from a Central Mixing Plan," *Proceedings*, ASTM, Vol 31, Part II (1931).

[12] British Standards Institution, "Methods of Testing Concrete," BS 1881:1952.

[13] DIN 52171, "Stoffmengen und Mischungverhaltnis im Frisch-Mortel und Frisch-Beton" (Material Quantities and Mix Proportion in Fresh Mortar and Concrete) (German Standard, 1961).

[14] MNOSZ 4714 T, "Friss betonkeverek vizsalata," (Methods of Testing for Fresh Concrete), Magyar Nepkoztarsasagi Orszagos Szabvany Tervezet (Hungarian Standard, 1955).

reported their views on this method or on some of its modifications with varying degrees of support.[15,16,17,18,19]

The test method specified in B.S. 1881: Part 2: 1970, was essentially developed by Kirkham[20] and is a variant of the Dunagan method. It requires that the analysis of the concrete be supplemented by tests on the fine and coarse fractions of the aggregate concerning specific gravity, absorption, and grading. The weights of fine and coarse aggregate are determined by weighing in water, and the weight of cement is obtained as a difference between the weight in water of concrete and of the aggregates.

A variant of this method is when the particles passing the sieve No. 199 (0.15 mm) are collected into a container and their weight is determined directly rather than as a difference.[21,22] In other variants, the material wet-screened through sieve No. 100 is separated out by filtering and pressing dry.[23]

A recent mechanized apparatus begins with the elutriation of a weighed sample of concrete with water, whereby cement and other fine particles are separated as a slurry. This is followed by sub-sampling, flocculation, and measurement of the cement by weight in a constant volume vessel. The process reportedly takes 5 minutes.[24]

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[15] Thaulow, S., "Field Testing of Concrete," (Norsk Cementforening, Oslo, 1952).

[16] Vollick, C. A., "Uniformity and Workability," *Significance of Tests and Properties of Concrete and Concrete Making Materials*, ASTM Special Technical Publication No. 169-A, (1968), pp 73-89.

[17] Covault, D. O., and Poovey, C. E., "Use of Neutron Activation to Determine Cement Content of Portland Cement Concrete," *Construction of Concrete Pavement*, Bulletin 340, Highway Research Board (1962), pp 1-29.

[18] Lorman, W. R., "Plastic Concrete Quality Control," *Technical Note* N-395 (U.S. Naval Civil Engineering Laboratory, 1961).

[19] Lorman, W. R., "Verifying the Quality of Freshly Mixed Concrete," *Proceedings*, ASTM, Vol 62 (1962), pp 944-959.

[20] Kirkham, R.H.H., "The Analysis of Fresh Concrete," *Concrete and Constructional Engineering*, (February 1949).

[21] Laing, J., "Simple but Precise Method for the Rapid Analysis of Fresh Mixed Concrete," *RILEM Bulletin*, No. 22, (New Series) (Paris, March 1964), p 59.

[22] Turton, C. D., "Rapid Analysis of Freshly Mixed Concrete," *Engineering*, Vol 191, No. 4960 (May 12, 1961), p 659.

[23] Bavelja, R. A., "A Rapid Method for the Wet Analysis of Fresh Concrete," *Concrete*, Vol 4, No. 9 (September 1970), pp 351-353.

[24] Forrester, J. A., and Lees, T. P., *Apparatus for the Rapid Analysis of Fresh Concrete to Determine its Cement Content*, *Technical Report* No. 42.490 (Cement and Concrete Association, London, 1974), pp 15.

Another method is based on determining the density of a cement suspension.[25] After washing a sample of fresh concrete over a No. 100 sieve, hydrometer readings are recorded of the suspension collected. By reference to a control curve obtained from hydrometer readings of water in which known quantities of cement are suspended, the amount of cement can be determined.

In all these methods calculation of the cement weight has to include a correction for the silt and dust in the aggregate as determined by a sieve analysis on the aggregate samples. Other methods for the separation of cement and very small aggregate particles utilize the difference in the specific gravity of the two materials by applying a suitable heavy media and/or centrifugation.[26,27,28,29] The centrifuge test appears more suitable for laboratory investigations of a mixer performance than as a field test for cement content.

Another method developed by Kelly and Vail[30] also begins with wet sieving. A set of two sieves, No. 4 (4.75 mm) and No. 50 (0.30 mm) are arranged over a single tub washing machine which has an impeller type agitator and a pump to circulate the contents continuously via an outlet hose through the sieves. A kilogram (2.2 lbs) of fresh concrete is placed in the top sieve and the machine is filled with a known volume of water. The cement and sand are separated from the coarse aggregate by the jet of water coming from the hose, and the material passing the No. 50 sieve is held in suspension by the agitator and continuous circulation. This slurry is sampled by an automatic pipette system which contains a dispenser for a measured quantity of nitric acid. The sample and nitric acid are washed with a known volume of water into a mixing cup where the contents are stirred vigorously and an acid

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[25] Murdock, L. J., "The Determination of the Properties of Concrete," *Cement and Lime Manufacture*, Vol 21 (1958), pp 91-96.

[26] Hime, W. G., and Willis, R. A., "A Method for the Determination of the Cement Content of Plastic Concrete," *ASTM Bulletin*, No. 209 (October 1955), pp 37-43.

[27] Walker, S., Bloem, D. L., Gaynor, R. D., and Wilson, J. R., "A Study of the Centrifuge Test for Determining the Cement Content of Fresh Concrete," *Materials Research and Standards*, ASTM, Vol 1, No. 6 (June 1961).

[28] Bloem, D. L., Gaynor, R. D., and Wilson, J. R., "Testing Uniformity of Large Batches of Concrete," *Proceedings*, ASTM, Vol 61 (1961), pp 1119-1140.

[29] Kelly, R. T. and Vail, J. W., "Rapid Analysis of Fresh Concrete," *Concrete* (April 1968), p 140, (May 1968) p 206.

[30] Howdyshell, P. A., *Evaluation of a Chemical Technique to Determine Water and Cement Content of Fresh Concrete*, Presented at the 54th Annual Meeting of the Transportation Research Board, Washington, D.C., January, 1975.

solution is produced. An aliquot of the solution is taken and its calcium content is measured by means of a flame photometer, calibrated with a known acid solution of cement. This technique is sensitive to the type of aggregate, especially when the concrete contains limestone in significant quantity. Otherwise the Kelly-Vail method appears to be a good practical method for the determination of cement content.[31] Other methods of treating cement may also be considered, such as complexing it in organic acids or weak inorganic acids that leave calcium carbonate unattacked but these need further research.

Two additional physicochemical methods for determining the cement content were developed by Chadda.[32] In the first method, the cement content is estimated by an electrical conductimetric method based on the determination of conductivity of water in which known quantities of unset cement-sand mixture have been shaken. From a standard curve showing the relationship between cement concentration and conductivity, the cement content of a sample can be interpolated from its conductivity measurement. The second method for determining the cement content is based on the differential absorption characteristics of cement and sand particles. The percent absorption increases as the concentration of cement increases in the mixture. However, the applicability of these methods has yet to be established. One can reason, for instance, that the conductivity of a fresh concrete depends perhaps more on the water content than on the cement content.

Another principle, suggested by Popovics,[33] involves testing the same batch of concrete by two different consistency tests, e.g., the penetration test and the remolding test. Pertinent formulas indicate that if the penetration measure of the concrete is, say, 4 in. (10 cm), and its remolding measure is around 20, then this concrete has a high cement content; if, however, its penetration measure is still 4 in. but the remolding measure is around 40, the concrete has a low cement content. Unfortunately, the practical application of this principle is not reliable enough when the presently standardized methods for measuring consistency are used, due to the high random variations of the results of these tests. It is possible, however, that other consistency tests can provide more reliable results.

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[31] Howdyshell, P. A., *Evaluation of a Chemical Technique to Determine Water and Cement Content of Fresh Concrete*, Presented at the 54th Annual Meeting of the Transportation Research Board, Washington, D.C., January, 1975.

[32] Chadda, L. R., "The Rapid Determination of Cement Content in Concrete and Mortar," *Indian Concrete Journal* (August 15, 1955), pp 258-260.

[33] Popovics, S., "Consistency and Its Prediction," *RILEM Bulletin*, No 31 (Paris, June 1966), pp 235-252.

DETERMINATION OF THE WATER CONTENT AND WATER/CEMENT RATIO

The earliest and simplest method for the determination of water content of fresh concrete is to weigh a fresh concrete sample, then dry it out by heating, weigh it again, and accept the weight difference as the water content of the sample. This method is rather time consuming and yet not very accurate.[34] Another method specified in the B.S. 1881 determines the water as the difference between the weight of the fresh concrete sample in air and the calculated weight of all solids in air. This method is not accurate enough either under practical circumstances.

Chemical methods are also suitable for determination of the water content. For instance, the amount of acetylene produced when an excess amount of calcium carbide is added to the fresh concrete sample can be used to calculate water content. In the Kelly-Vail method the water content of fresh concrete is measured by observing the dilution of chloride ions when a measured volume of a standard sodium chloride solution is mixed with the concrete sample.[35] Although this test is again sensitive to the type of aggregate used, Howdyshell found the results of this test representative of the water content, especially of the amount of free water in the mixture.[36]

Several other methods potentially suitable for the determination of water content are reviewed by Monfore[37] as follows:

Thermal Conductivity Methods. The usual procedure is to heat a slender specimen by means of an electric current and measure the rate at which the temperature of the specimen increases. The higher the water content in the specimen, the slower the temperature rise. Calibration of equipment may be done in terms of water content.

Capacitance Methods. The dielectric constant of water is much higher than that of the dry constituents of concrete. Thus, the higher

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[34] Forrester, J. A., "Review of Techniques for the Rapid Analysis of Fresh Concrete," *Departmental Note*, DN/4008 (Cement and Concrete Association, London, October 1968).

[35] Kelly, R. T. and Vail, J. W., "Rapid Analysis of Fresh Concrete," *Concrete* (April 1968), p 140 (May 1968) p 206.

[36] Howdyshell, P. A., *Evaluation of a Chemical Technique to Determine Water and Cement Content of Fresh Concrete*, Presented at the 54th Annual Meeting of the Transportation Research Board, Washington, D.C., January, 1975.

[37] Monfore, G. E., "A Review of Methods for Measuring Water Content of Highway Components in Place," *Highway Research Record No. 342, Environmental Effects on Concrete* (Highway Research Board, 1970) pp 17-26.

the water content, the greater the dielectric constant of the fresh concrete becomes. The capacitance may be influenced by the presence of salts in the water.

Microwave-Absorption Methods. The absorption of electromagnetic radiation by a material is a function of the dielectric constant, thus this method is closely related to capacitance methods. Measurements are made by determining the attenuation of the radiation as it passes from the transmitting horn antenna through the specimen to the receiving horn antenna. Calibration of the equipment for differing mixtures may be necessary.

Electrical Resistance Methods. The electrical resistance of concrete decreases with the increase in the water content. However, direct measurement of the resistance can provide erroneous data for the estimation of the water content in the concrete due to variations in concentration of soluble salts. Such errors may be lessened by embedding the electrodes in gypsum, and then embedding the gypsum block in the fresh concrete. Thus, the water content may be calibrated in terms of the electrical resistance of the gypsum block.

Finally, the water content of a fresh concrete sample can be estimated by repeated consistency tests.[38] The steps applied for the slump test are as follows:

1. Determine the y_1 slump of the concrete sample

2. Mix a known w_0 amount of water to the concrete sample and determine tye y_2 slump of this new concrete

3. Calculate the original w_1 water content as

$$w_1 = \frac{w_0}{(y_2/y_1)^{0.1} - 1}$$

Here again the random variations of the results of slump test are so high that the calculated w_1 value is not reliable enough. It is possible, however, that other, more reproducible consistency tests would provide an acceptable estimate for the water content.

The water/cement ratio can be calculated from the actual cement content and water content of the fresh concrete sample determined by

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[38] Popovics, S., "Consistency and Its Prediction," *RILEM Bulletin*, No. 31, (Paris, June 1966), pp 235-252.

any of the methods discussed earlier.[39] Methods have also been proposed for the direct estimation of the w/c ratio in the fresh concrete. Since, however, these methods require the knowledge of the cement content, or the mix proportion, of the sample for the calculation of the water/cement ratio, they determine in reality the water content of the sample. That is, these methods do not differ significantly from the methods discussed above.

One such a method, recommended by Thaulow[40], calculates the water/cement ratio from the mix-proportion and from the weights of an air-free concrete in air and under water since the weight of the water in the concrete under water is zero. A variant of this method was recommended by Orchard.[41] Incidentally, a similar method is specified in ASTM C 70 - 772 for the rapid determination of the surface moisture in fine aggregate.

Attempts have also been made to determine the water/cement ratio by electrical resistance methods.[42,43] Here again such measurements do not evaluate the water/cement ratio in reality but rather the water content as compared to a previously calibrated sample. If the cement content is known, this method can provide the water/cement ratio with an accuracy of ±0.5.[44]

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

Despite the large amount of literature available on analyzing the composition of fresh concrete, no definite conclusion can be drawn on which method is best for the practical determination of cement and water contents. Since the pertinent experiments are limited and were performed under varying conditions, no meaningful comparison can be made between the reported, sometimes conflicting results. Among the

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[39] Robertson, J. A., and Colquhoun, R. S., "'Instant' Testing of Concrete Mixes," *Civil Engineering and Public Works Review*, Vol 64, No. 754, (May 1969), pp 453-456.

[40] Thaulow, S., "Field Testing of Concrete," (Norsk Cementforening, Oslo, 1952).

[41] Orchard, D. F., "The Effect of the Vacum Process on Concrete Mix Design," *Symposium on Mix Design and Quality Control of Concrete* (Cement and Concrete Association, London, May 1954), pp 107-131.

[42] Anon., "New Instrument Tests on Concrete Mix; Water-Cement Ratio Found Electrically," *Engineering News-Record*, Vol 150, No. 25 (1953), p 51.

[43] Naray-Szabo, I., and Szuk, G., "The Determination of the Optimal Water-Cement Ratio of Concrete by Electrical Means," *Acta Geologica*, Vol III, No. 1-3 (Budapest, 1955), pp 105-114.

[44] Lorman, W. R., "Verifying the Quality of Freshly Mixed Concrete," *Proceedings*, ASTM, Vol 62 (1962), pp 944-959.

nonnuclear test methods, some of the variants of the Dunagan and Kelly-Vail methods have perhaps been most supported in the literature.

To establish a more definite judgment concerning the values of the test methods discussed in this paper, a comparative investigation is necessary which covers the most promising methods for determination of the cement and water contents, or possibly the water/cement ratio, of fresh concretes. This should include, of course, some of the nuclear methods. Another area of future research is to improve the existing methods and possibly to develop new, better methods.

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THE KELLY-VAIL CHEMICAL TECHNIQUE FOR WATER AND CEMENT CONTENT

by

R. T. Kelly
P. J. Baldwin

Greater London Council Scientific Branch

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RAPID TESTING OF FRESH CONCRETE
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ABSTRACT

A chemical method of determining the cement and water content of fresh concrete on site, within 15 minutes of sampling, is described. The choice of analytical equipment and technique is outlined and details of the development given. The precision and accuracy of the method under laboratory and site conditions are evaluated and a site trial described. The experience of other users of the technique is reviewed and the limitations of the method discussed. Full analytical details of the method are given in the Appendix.

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INTRODUCTION

Traditionally, the methods used on construction sites in the United Kingdom for evaluating the quality of concrete are tests for slump, density, and strength in compression of test cubes. The limitations of these methods when applied to the day-to-day quality control of concrete placed on site are well established. In particular the cube test suffers two major deficiencies:

1. It is nonspecific

2. There is a considerable time-lag between the concrete being placed and the availability of test results.

Experience within the Greater London Council (GLC) over a number of years has shown that chemical analysis of cubes which had shown some anomaly in the compressive strength test could reduce the limitations imposed by the first of these deficiencies, but would add to the delay.

As a result of this work it seemed desirable to develop a method which would analyze concrete before placing and hardening rather than after the cube test results had been obtained. Such a method should at the very least determine the cement content, since this is clearly a key factor not only in strength attainment of the concrete but also in its long-term durability. Preferably the method should also be capable of estimating the water/cement ratio.

The approach by the GLC Scientific Branch in developing the techniques described by R. T. Kelly and J. W. Vail[1] used the experience gained in hardened concrete analysis and also took consideration of the following:

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[1] Kelly, R. T. and Vail, J. W., "Rapid Analysis of Fresh Concrete," *Concrete* (April 1968), pp 140-145, (May 1968), pp 206-210.

1. The personnel available for the laboratory development were essentially analytical chemists by training

2. Only very limited engineering workshop facilities were available

3. The technique evolved should be rapid (on the order of 10-15 minutes); cheap in manpower, equipment, and materials; capable of site operation; and present no significant safety hazard.

DEVELOPMENT OF THE METHOD FOR CEMENT DETERMINATION

Consideration was given to the use of the method described in BS 1881 Part 2. The Scientific Branch had no experience of this method as a site test, but its use was rejected because it was understood to require up to 1 hour to complete, and required samples of the aggregates for calculation of correction factors. These samples could not readily be made available on Council sites. However, the principle of separating the coarse material from the cement and fine sand by washing the sample through a nest of sieves was adopted. Experimentation showed that a uniform suspension of the resulting cement/sand/water slurry could be effected by powerful agitation and rapid recirculation. The feasibility of obtaining a suitable sub-sample of the suspension was also established.

In order that the cement content of the suspension could be determined quickly it was felt that a chemical analytical technique would have to be used. It was not considered possible to use the well established gravimetric or volumetric techniques and flame photometry was the only choice capable of reaching the required speed of operation. To use this it was necessary to avoid the delay inherent in the usual sample dissolution techniques employed in cement analysis. It was therefore necessary to establish that quantitative dissolution could be effected by rapid stirring in the cold. Chemical determination of the calcium oxide contents of solutions prepared by stirring 1 g samples of cement with cold nitric acid in a high speed mixer for varying periods of time established its feasibility.

Description of the Apparatus

A diagram of the apparatus which was developed for the preparation and sampling of cement/water suspensions is shown in Figure 1. In addition to the provision of powerful agitation and recirculation of a relatively large volume of suspension it was considered that the apparatus for preparation of the suspension should be robust and simple

to operate, resistant to corrosion by alkaline solutions and scouring by fine sand, and have no recesses in which cement could accumulate. All of these requirements were provided in a domestic single-tub washing machine with side agitation. Provision for sampling of the suspension is effected by a 125 ml glass pipette (with automatic levelling device) fitted with a two-way tap. Discharging through this pipette is a 100 ml automatic dispenser which enables the sampling pipette to be flushed out with a known volume of acid. A further 300 ml dispenser discharges directly into the cup of an ordinary domestic high speed stirrer and allows direct dilution of the test solution.

Method of Analysis for Cement Content

Full details of the analytical procedure are given in the Appendix; however, the major steps may be summarized as follows.

The tub of the agitator is filled with a known volume of tap water and the agitator and pump started. Approximately 1 kg of concrete sample is placed on the nest of sieves and washed until visually free of cement by spraying water from the recirculating hose. After 3 minutes' agitation and recirculation of the suspension, the stream from the hose is diverted into the pipetting device until it is just filled. The sub-sample is drained into the mixer cup and the pipetting device flushed through with nitric acid from the 100 ml dispenser. The dilution water is added and dissolution effected by stirring the contents of the mixer cup for 3 minutes. The calcium content of the solution is measured on a flame photometer calibrated with tap water and standard calcium solution immediately prior to measurement. Cement content is determined by reference to a previously constructed calibration curve.

The average time taken for these operations by an experienced operator was found to be just over 7 minutes.

Experimental Verification of the Method for Cement Determination

During development of the method described above, a number of factors were investigated.

1. Efficiency of preparation of cement suspension in water. Known weights of cement were slurried with water and added directly to the water in the agitator tub. Samples were withdrawn from different parts of the system after varying intervals of time. Determination of the cement content of these, by analysis for calcium oxide, established that a suitably homogeneous suspension was obtained after 3 minutes and that this could be satisfactorily sampled via the recirculating hose.

2. Calibration of flame photometer. Standard solutions prepared by dissolving cement in cold nitric acid (1 percent V/v) gave a highly reproducible calibration curve provided that measurement was made within two hours of dissolution. Difficulties were experienced in preparing flame photometer calibration standards with adequate stability over long periods of time. These were overcome by using calcium carbonate solutions as standards. Tap water was used in the preparation of all the standard solutions.

3. Determination of the cement content of test mixes. To determine the performance of the whole apparatus, the cement contents of samples of known composition were determined by the method given in the Appendix except that varying weights of samples were analyzed. The mixes were prepared from weighed quantities of washed, dried aggregate, tap water and ordinary portland cement, and the whole of the mix was analyzed. The flame photometer was calibrated with the cement used for the mixes. The results obtained are given in Table 1.

In the majority of cases two samples of suspension were taken for each mix and analyzed for cement content separately.

DEVELOPMENT OF THE METHOD FOR WATER DETERMINATION

Pilot investigations showed that the more obvious physical properties such as electrical conductivity could not be determined with sufficient accuracy by simple, inexpensive equipment. Drying techniques were found to be time-consuming. Extraction of the water by alcohol was shown to be feasible. Subsequent determination of the water content of the alcohol extract was possible using the Karl Fischer titration. The use of such a technique was rejected, however, since adequate accuracy could only be achieved by a skilled analyst using expensive and delicate apparatus. The method finally adopted was based on the assumption that the water in fresh concrete is available for intermixing with added aqueous solutions.

If a sample of concrete containing a volume of water A is intimately mixed with a volume B of an aqueous solution of strength S_1, then provided that the solute is not absorbed by either the cement or aggregate, the strength S_2 of the intermixed solution is related to the initial strength by:

$$B \times S_1 = (A+B)\ S_2$$

Thus if B and S_1 are fixed and S_2 is determined, A, the water content of the concrete, can be calculated.

To measure this dilution effect, it was decided to use sodium chloride as solute, it being cheap and its use having the additional

Table 1

Determination of Cement Content of Fresh Mixes

Mean recovery (39 determinations):96.9% Standard deviation: 3.2
Range of recoveries: 90.8% to 105.8% Coefficient of variation of recoveries: 3.3%

Weight of Wet Concrete (kg)	Nominal Mix Proportions (by weight)	Water/Cement Ratio	Actual Cement Content (g)	% Recovery
4.75	1 : 3 : 6	0.5	450	95.8, 97.9
1.62	1 : 1 : 2	0.5	360	103.8,100.3
3.37	1 : 3 : 6	0.5	320	95.9, 95.9
1.80	1 : 1½: 3	0.5	300	99.1, 99.1
1.85	1 : 2 : 4	0.4	250	97.3, 97.3
2.52	1 : 3 : 6	0.5	240	92.8, 90.8
2.12	1 : 3 : 6	0.6	200	101.0,105.8
1.90	1 : 3 : 6	0.5	180	101.6,101.6
1.90	1 : 3 : 6	0.6	180	94.5, 97.2
1.90	1 : 3 : 6	0.6	180	97.2, 97.2
1.90	1 : 3 : 6	0.6	180	97.2, 99.0
1.90	1 : 3 : 6	0.6	180	97.2, 97.2
1.90	1 : 3 : 6	0.6	180	97.2, 97.2
1.90	1 : 2 : 6	0.6	200	93.0, 93.0
1.90	1 : 2 : 6	0.6	200	93.0, 95.4
1.90	1 : 2 : 5	0.6	220	93.2, 93.2
1.90	1 : 2 : 5	0.6	220	97.5, 94.7
1.00	1 : 1 : 2	0.5	220	94.7
1.00	1 : 1 : 2	0.5	220	97.5
1.00	1 : 1 : 2	0.5	220	94.7
1.00	1 : 1 : 2	0.5	220	94.7
1.00	1 : 1 : 2	0.5	220	99.0

advantage that chloride ion in solution is readily determined by the Volhard back-titration method. To facilitate the chloride determination, constant volume dispensers were used.

Rapid intimate mixing of the added chloride solution and concrete sample was effected by using an end-over-end shaker of the type which has proved efficient for the examination of bituminous road materials.

Method of Analysis for Water Content

Full details of the method are given in the Appendix. Briefly, it consists of weighing out two separate 1 kg samples of the concrete and placing them in containers marked S and B. 500 ml of a salt solution of known strength are added to container S and 500 ml of chloride-free water are added to container B. The containers are sealed and the contents shaken for 3 minutes in an end-over-end shaker. The contents are allowed to stand for 3 minutes, samples of the supernatant liquid removed by pipettes and their chloride contents determined by Volhard titration. The water content of the concrete is calculated from the chloride content of container S after correction for the chloride content of B.

The average time taken by an experienced operator to complete this procedure was found to be 7 minutes 30 seconds.

Experimental Verification of the Method for Water Determination

In developing the method the following investigations were carried out.

1. Amount of sodium chloride and settling time. Experiments were carried out to determine the optimum concentration of the solution and the ratio of weight of concrete to added volume of solution. The greater this ratio the more sensitive the method, but the longer the settling time required to obtain a clear supernatant solution. It was shown that a convenient volume of solution to use was 500 ml per 1 kg of fresh concrete. The use of solutions of sodium chloride no weaker than N/2 was found to be advisable in order that a sharp titration end point could be obtained by back-titrating with potassium thiocyanate solution one-tenth of this concentration.

2. Time of mixing. Using the method described in the Appendix but varying the time of mixing, it was established that only 3 minutes of mixing in the end-over-end shaker was required to obtain sufficient intermixing of the salt solution and the water from the concrete.

3. Determination of the water content of test mixes. To assess the method's performance, the water contents of concretes of known composition were determined as described in the Appendix. The test mixes were prepared as for those used for verification of the cement method. The results obtained are given in Table 2.

The results suggest a possible trend to lower recoveries at higher aggregate/water ratios, probably due to the absorption of water by the oven-dried aggregates.

The results obtained for determinations made on 1 kg samples prepared to the same specification and individually analyzed are given in Table 3.

SITE EVALUATION OF THE RAPID ANALYSIS TECHNIQUE

To establish the feasibility of using the techniques developed under site conditions a 5-month trial was carried out on a large construction site in central London. The equipment was installed in part of a small weatherproof hut used by the contractor for the preparation of test cubes. Mains, electricity, water, and a drainage sump were provided. Bottle gas was used to operate the flame photometer.

Six mixes ranging from 1:4-1/2 to 1:16 nominal proportions, which were either delivered to or made on the site during the 5 months of the trial, were sampled and analyzed on a number of occasions. In addition, test mixes of known composition were analyzed so that site performance of the equipment could be compared with that in the laboratory. The test mixes were made from the same components as were used for the site concrete. The aggregate, however, was oven-dried before use. The whole of the test mix was analyzed to avoid sampling errors. Results of the test mixes are given in Table 4.

Performance of the Equipment

The apparatus for the cement determination was operated as described in the Appendix. In order that any faults in the apparatus might be diagnosed, cement/water slurries of known composition were analyzed daily. Recoveries of between 95 percent and 105 percent were considered to indicate that the apparatus was working efficiently. During the trial period only two small faults were shown up. Both occurred early in the trial and once corrected did not recur. The only aspects of the equipment operation which required particular attention were flushing out of the flame photometer atomizer with distilled water between each measurement, and flushing out of the agitator tub.

Table 2

Determination of Water Content: Range of Water Contents

(All samples 1 kg)

Nominal mix Proportions (by weight)	Actual Water Content (g)	% Recovery
1 : 3 : 5 : 0.4	43	87.7
1 : 3 : 5 : 0.4	43	89.9
1 : 1-1/2 : 3-1/2 : 0.7	107	97.9
1 : 1-1/2 : 3-1/2 : 0.7	107	96.7
1 : 1-1/2 : 3-1/2 : 0.7	107	96.4
1 : 1-1/2 : 3-1/2 : 0.7	107	97.0
1 : 2 : 2 : 1.0	166	97.6
1 : 2 : 2 : 1.0	166	97.6
1 : 1 : 2 : 1.0	200	98.4
1 : 1 : 2 : 1.0	200	98.4

Table 3

% Recoveries for Determination of Water Content

(All samples consisted of a nominal 1 : 1 : 2 : 0.35 containing 80 cc of water per kg of fresh concrete)

94.0	94.1	94.3	99.6
92.5	93.0	92.5	95.5
91.9	92.5	95.5	95.5
96.0	89.5	95.5	95.5

Mean recovery (16 determinations): 94.2%
Range of recoveries: 89.5% to 99.6%
Standard deviation: 2.3
Coefficient of variation of recoveries: 2.4%

Table 4

Analysis of Test Mixes

Weight of Fresh Concrete kg	Cement			Water		
	Added g	Found g	Recovery %	Added g	Found g	Recovery %
1	140	139	99	75	78	104
1	122	126	103	100	99	99
1	140	150	107	70	71	101
1	185	187	101	115	110	96
1	153	158	103	90	88	98
1	175	172	98	80	81	101
1	190	180	95	100	102	102
1	118	110	93	100	102	102
1	168	169	101	82	85	104
1	157	155	99	93	99	106
1	130	134	103	70	75	107
1	130	135	104	70	75	107
1	150	147	98	90	95	106
1	127	127	100	98	102	105
1	175	187	107	75	75	100
1.4	200	200	100	-	-	-
1.5	200	183	92	120	117	98
1.5	200	191	96	120	121	101
1.5	200	200	100	100	99	99
1.5	200	188	94	100	99	99
1.5	200	191	95	100	95	95
1	170	165	97	111	110	99
1	170	156	92	111	102	92
1	170	161	95	111	106	95
1	170	156	92	111	106	95
1	170	165	97	111	110	99
1	170	161	92	111	102	92
1	150	143	95	90	92	102
1	183	191	104	-	-	-
1	183	183	100	-	-	-
1	140	150	107	70	71	101
1	122	126	103	100	99	99
1	185	187	101	115	110	96

Cement determinations:		Water determinations:	
Mean recovery (33 determinations)	99%	Mean recovery (30 determinations)	100%
Range of recoveries	92-107%	Range of recoveries	92-107%
Standard deviation	4.6%	Standard deviation	4.1%
Coefficient of variation of recoveries	4.6%	Coefficient of variation of recoveries	4.1%

No difficulty was experienced in performing the water content determination as described in the Appendix.

Sampling

Several difficulties were encountered in sampling the ready-mixed concrete delivered to the site. Since the delivery schedule was dictated by the building requirements, the analyst had no prior knowledge of the exact arrival time of a lorry, how soon after arrival it would discharge its load, or the length of time it would take to discharge. Attempts to randomize sampling on a formal basis were therefore not possible.

The procedure adopted was to take either one or two samples per load by holding a plastic bucket in the concrete stream during discharge. The point from which the sample was taken (i.e., early, middle, or late in the discharge) was estimated after discharge was complete. Approximately 20 lb of concrete was taken for each sample. The whole of this sample was remixed before sub-sampling for cement and water determinations.

Results

Only two of the mixes used on the site were sampled in sufficient numbers to allow meaningful statistical analysis of the results obtained. These were nominally 1 : 1-1/2 : 3 and 1 : 2 : 4 by volume. Both were delivered to the site as ready-mixed concrete or were made on site.

An analysis of variance was carried out on the results so that the contributions of within-sample variation and within-batch variation to the overall variability might be assessed. Because of the sampling difficulties encountered with delivered concrete it was only possible to get sufficient data for determination of the within-sample variation for site-mixed concrete. For the purpose of analysis of the results it was assumed that the within-sample variation for ready-mixed concrete would be identical.

The within-sample variation was found to be the same order as the analytical error obtained for test mixes. The main source of error at sub-sampling level is therefore analytical error.

The overall within-batch variations include those arising from mixing efficiency and within-sample variations. Analysis of the data showed that the differences between the mean values of samples taken from early, middle or late in the discharge were not significant

(at the 95 percent confidence level) for either ready-mixed or site-mixed concrete. Thus, despite observed variations throughout the load, there was no apparent trend toward segregation in the mixer or during transport. The calculated overall within-batch variations are shown in Table 5.

Table 5

Within Batch Variations

	Mix 1		Mix 2	
	Water content (g kg)	Cement content (g kg)	Water content (g kg)	Cement content (g kg)
Ready-mix				
Standard deviation	5.8	11.1	5.3	6.3
Mean	78	121	81	103
Coefficient of variation	7.4%	9.2%	6.5%	6.1%
Site mix				
Standard deviation	3.5	9.1	6.0	4.6
Mean	87	144.5	79	119
Coefficient of variation	4.0%	6.3%	7.6%	3.9%

The importance of these figures is that they permit calculation of the lowest number of samples required to be analyzed if the estimated mean value for the mix is to fall within stated limits of the true value. For example, from the data obtained it was shown that the estimated mean values for the 1 : 2 : 4 mix would fall within 40 lb/yd^3 for the cement and within 20 lb/yd^3 for the water if six separate samples were taken throughout the mix and the composition of the combined samples determined after blending.

EXPERIENCE OF OTHER WORKERS USING THE CHEMICAL TECHNIQUES

Since the chemical technique was proposed by Kelly and Vail in 1968, a number of evaluations of the method have been carried out. In 1973 A. C. Edwards and G. D. Goodsall[2] reported on a field

[2] Edwards, A. C. and Goodsall, G. D., *Field Investigation of a Method for the Rapid Analysis of Fresh Concrete*, Transport and Road Research Laboratory Report LR 560 (1973).

investigation of the technique. They examined one mix, designed to have an aggregate/cement ratio of 3.93 and water/cement ratio of 0.47. The aggregate was quartzite-gravel and its maximum size was 20 mm (3/4 in.).

Four increments were taken from different parts of the load to form each sample and two samples of about 20 kg were taken from each $3m^3$ load delivered. 1 kg sub-samples were obtained by coning and quartering techniques so that two cement determinations and two water determinations were carried out for each sample. 10 loads were reported on.

It was concluded that the repeatability of the cement determination was 2 percent of the total mix and that of the water determination 1 percent of the total mix. These were considered by the authors as suitable for assessing concrete under site conditions. The cement and water contents could be determined in 15 minutes.

In July 1974 P. A. Howdyshell[3] reported on a laboratory evaluation of the Kelly-Vail technique. Investigations were designed to assess the effect of aggregate type, aggregate moisture content, cement type, and length of mixing time on the water content determination; and the effect of aggregate type and aggregate grading on the cement content determination.

The investigations confirmed that the chemical procedure was capable of determining cement and water content of fresh concrete within about 15 minutes. They further indicated that the results obtained could be used to predict strength potential of the concrete. Aggregate type was shown to have a significant influence on the test results, but the influence of aggregate moisture condition, mix proportions and length of mix time were less significant. Even though the method was sensitive to aggregate type, satisfactory results were obtained for concrete made from both gravel and limestone aggregate. It was considered that the test results for water were a better measure of free water than total water.

Experience gained by other workers has shown that several problems have been encountered. Cement content determinations have been reported as unsatisfactory when calcareous aggregate has been used and where the calcium content of cement has varied considerably. The small sample size used has presented sampling problems when the maximum aggregate size has been greater than 20 mm (3/4 in.). Few difficulties have been experienced with the water content determination although the use of nitrobenzene on site has been considered undesirable by some workers.

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[3] Howdyshell, P. A., *Laboratory Evaluation of a Chemical Technique to Determine Water and Cement Content of Fresh Concrete*, Interim Report M-97 (Construction Engineering Research Laboratory, July 1974).

DISCUSSION

Difficulties associated with the use of the technique for cement content determination of concrete containing calcareous aggregate may be minimized in many cases. In the London area much of the aggregate containing calcareous material used for structural purposes is sea-dredged and the calcareous content is in the form of shell. Work has shown that when marine sands (which may contain up to 30 percent by weight of shell as calcium carbonate) are processed without being incorporated in a concrete mix, by the technique for cement content determination the reading obtained on the flame photometer is very low. Howdyshell and other workers have shown that, where representative samples of calcareous aggregates are available, suitable blank determinations can be carried out and meaningful corrections made to the determined cement content. Where representative samples of aggregate are not available it may be possible, in those cases where the calcium content of the aggregate is essentially calcium carbonate, to carry out a rapid volumetric carbonate determination. However, it is considered that at the moment this would need to be done by a more experienced analyst than is required for the other procedure. However development of a technique requiring less analytical skill is a possibility. Where difficulties arise from the variations of calcium content of cement it may be possible to make allowance if detailed knowledge and/or representative samples can be obtained, although difficulty in obtaining such information on Council sites was one of the reasons for developing the method in the first place.

Errors due to the sampling difficulties imposed by the use of aggregates larger than 20 mm may be reduced by modifying the technique for cement content. During development of the technique the question of sample size was investigated. The upper limit on the sample weight is governed to some extent by the need to prevent blocking of the nest of sieves. If however a number of separate samples are processed in sequence through different nests of sieves then the cement from several 1 kg samples may be collected in the tub of the agitator. Experimentation has shown that up to 10 g/liter of cement may be suspended and subsequently sampled by the apparatus.

Experience in the GLC Scientific Branch over a number of years has shown that the precision of the water content determination is improved by use of burettes for the titration of chloride. However, their use would require a more experienced operator and a number of disadvantages of the method would still remain. Among these disadvantages are:

1. Very large volumes of reagents are required
2. A laboratory back-up is essential
3. The use of silver nitrate is very expensive

4. The reagents for Volhard titration are highly toxic.

It is felt that use of a coulometric titration technique employing an automatic instrument overcomes many of these disadvantages. Only a few milliliters of reagent are required for each determination, the method is quicker, requires less operation time and, being automatic, is much less dependent on operator skill.

During the development of the original water determination method, the need to determine a materials blank in order to allow for adventitious chloride was considered an unavoidable complication if the other requirements were to be met. However there has been increasing use of marine aggregate in the London area over the past few years. A GLC specification limits the salt content of such aggregates and so the blank determination has been of increasing use in monitoring the salt contents of fresh concrete containing marine aggregate. Additionally, there is renewed interest in the control of the use of calcium chloride in concrete and the blank determination is of value in relation to this.

CONCLUSIONS

The chemical techniques for rapid determination of cement and water contents of fresh concrete on site proposed by Kelly and Vail have been shown by a number of workers to have application. They may be used:

1. As an acceptance test that allows rejection of concrete not complying with specifications before it is placed

2. For the day-to-day quality control of concrete

3. As a check on mixer efficiency

4. As a means of monitoring the amount of chloride either deliberately added as calcium chloride or present adventitiously when derived from marine aggregate.

Restrictions on their use may be imposed by some aggregate types, aggregate size, and extensive variations of the calcium content of the cement used.

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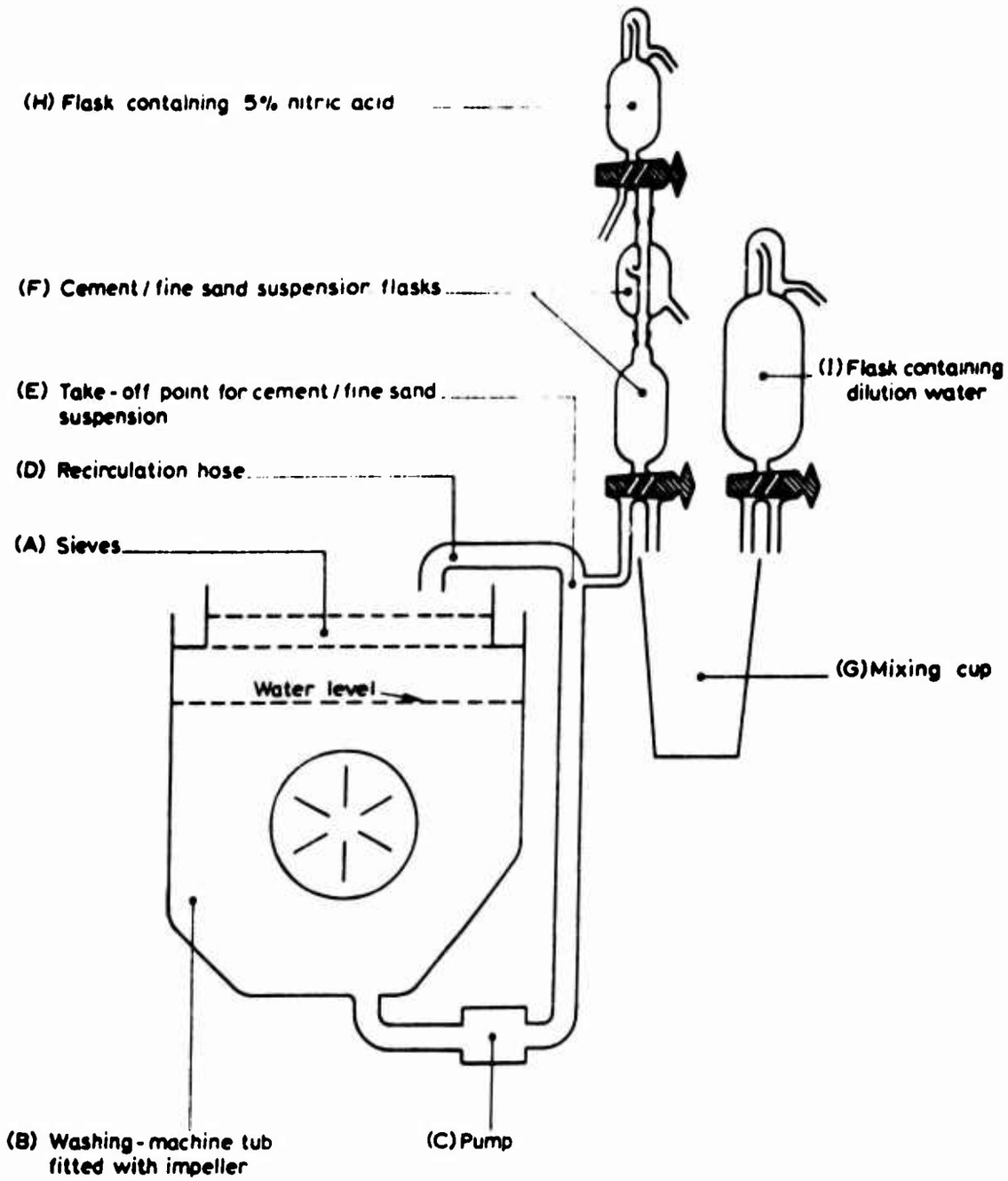

Figure 1. Diagram of equipment for preparing and sampling cement/fine sand suspension.

APPENDIX

THE ANALYSIS OF FRESH CONCRETE - SITE METHOD AND EQUIPMENT*

REAGENTS (normally prepared in the base laboratory and supplied to site as required)

Cement Determination

1. 5 percent Nitric Acid Solution - 5 ml HNO_3 (S.G.1.42) made up to 100 ml with tap water.

2. Tap water.

3. Standard Cement Solution - Take 1.2500 g fresh cement. Add sufficient tap water to form a slurry. Wash into the cup of a blender. Add 10 ml HNO_3 (S.G.1.42). Mix for 3 min. Make up to 1000 ml in a graduated flask with tap water. Mix well. *Do not use after two hours old.* With appropriate dilutions this standard is used to prepare a calibration curve as required.

4. Standard Calcium Solution - Take 1.60 g of dried $CaCO_3$. Place in a 250 ml beaker. Cover the $CaCO_3$ with tap water. Add 10 ml HNO_3 (S.G.1.42) carefully and cover the beaker immediately. When dissolved, transfer to a 1000 ml graduated flask; using tap water wash out the beaker and rinse the watchglass, adding the washings to the graduated flask. Make up to volume with tap water.

This solution is then adjusted in strength until it gives a reading of 100 on the flame photometer when the instrument has been set to read 100 using a freshly prepared standard cement solution containing 1.25 mg cement/ml (see above). Once adjusted this solution is used for the day-to-day checking of the maximum deflection setting of the flame photometer.

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* for noncalcareous aggregates

Water Determination

1. Nitrobenzene A. R.

2. Ferric Alum Solution (sat'd).

3. Silver Nitrate Solution approximately N/2 in distilled water.

4. Sodium Chloride Solution approximately N/2 in tap water.

5. Potassium Thiocyanate Solution approximately N/20 in distilled water.

6. 50 percent Nitric Acid Solution in tap water.

The final concentrations of solutions 3, 4, and 5 are *exactly* adjusted to the ratio 1:1:10 respectively, and checked by titration.

APPARATUS

Cement Determination

1. Single tub washing machine, fitted with a nest of two sieves (3/16 in. and 52 mesh) over the tub. Vigorous stirring of contents of tub by submerged impeller and recirculation by pump through a hose. T-piece in hose connected to automatic pipette. Working capacity of tub 37.6 liters.

2. Linked pipette assembly: 125 ml for sampling cement suspension; 100 ml for nitric acid; 300 ml for dilution water.

3. High speed stirrer - domestic pattern (milkshake type).

4. EEL flame photometer - operating from compressed air pump and Calor gas supply.

5. 5- and 10-liter containers for reagents.

Water Method

1. End-over-end mechanical shaker - fitted with two cylindrical steel cans of approximately 3 liter capacity.

2. Four "Zipette" dispensers--10 ml, 5 ml, 2.5 ml, 2 ml; two 50 cc pipettes; one 100 ml burette; Conical flasks; two 500 ml graduated flasks.

PROCEDURE

Cement Determination

1. Fill the washing machine to the mark in the tank, i.e., with 37.6 liters of tap water.

2. Charge the automatic pipettes with their appropriate reagents, i.e., 300 ml of tap water and 100 ml of 5 percent nitric acid solution.

3. Start the flame photometer, warming up in the following manner: (a) *Turn on compressed air supply first* (when using Calor gas supply). (b) Turn on Calor gas and ignite. Note: Reverse of usual starting procedure for the EEL Flame Photometer is necessary if Calor gas is used otherwise this heavier gas accumulates in the photometer and is suddenly flushed out by draughts and flares dangerously on ignition.

4. Mix contents of bucket or other sample container. Weigh out 1 kg of fresh concrete to the nearest gram.

5. Transfer the weighed concrete to the sieves placed over the washing machine, switch on washing machine and wash the residue on the balance scoop into the washing machine using the jet of water from the recirculating pump hose.

6. Wash the +3/16 in. aggregate carefully, using the jet of water from the recirculating pump hose. When cleaned remove +3/16 in. sieve (should take about 1 minute).

7. Wash the +52 aggregate (for about 1 minute). Keep the jet of water moving slowly over the surface of the sieve to avoid loss of the suspension by splashing.

8. Remove 52 mesh sieve. Place pump hose into holder provided and allow suspension to mix for a further few minutes. The minimum total time for washing and mixing is 3 minutes; the maximum is 6 minutes.

9. Take aliquot using automatic pipette (125 ml) by placing a finger over the larger bore of the T-piece on the end of the pump hose, directing the suspension into the automatic pipette.

When the pipette is full *remove finger* and switch off lower pipette tap simultaneously.

10. Run the 125 ml aliquot of the suspension into the mixer cup. Wash out the automatic pipette using the 100 ml of 5 percent nitric acid solution contained in the automatic pipette fitted above the sample pipette. These washings also run into the mixer cup. Add 300 ml of the tap water from the appropriate automatic pipette.

11. Fix cup to high speed stirrer and stir for 3 minutes to ensure complete solution of cement.

12. Use tap water to set zero and standard calcium solution to set 100 on the flame photometer; record the photometer reading for the sample solution, flushing the instrument with distilled water between each reading. The reading for the sample solution is converted by the calibration curve previously prepared to a value A mgm cement/ml of final solution.

$$\% \text{ Cement on wet mix} = A \times \frac{\text{volume of aliquot + acid + dilution water}}{\text{Volume of aliquot}} \times \frac{\text{Volume of water in mixing tub}}{10{,}000}$$

13. At regular intervals check that the equipment is operating satisfactorily by analyzing a sample of wet concrete containing a known amount of cement. If the recovery is less than 95 percent or more than 105 percent a systematic check by laboratory staff of each stage of the analytical process will be necessary.

Water Determination

1. *Weigh two 1 kg samples of fresh concrete to the nearest gram.* Transfer one of the samples to a *dry* mixing can. Wash the contents of the scoop into the mixing can with 500 ml of distilled water. Fix on the lid and secure. This sample is the blank *required* for estimation of chloride in the concrete itself.

2. Wipe the scoop dry. Take the second 1 kg sample and transfer to the second dry mixing can. Wash the contents of the scoop into the mixing can with 500 ml of the approximate N/2 sodium chloride solution. Allow scoop to drain free of solution. Fix on the lid and secure.

3. Fix the two cans onto the end-over-end shaker securely and mix for 3 minutes (minimum).

4. Remove the cans from the shaker and allow to settle for 3 minutes (minimum).

5. Transfer 50 ml of the clear *sample* solution (by means of a pipette) into a 500 ml flask (conical) containing 50 ml (pipetted) of silver nitrate solution. Add 10 ml 50 percent nitric acid solution from a Zippette dispenser and mix. Add 2 ml of nitrobenzene (Zippette dispenser) and shake well to coat the silver chloride precipitate. Add 5 ml of ferric alum solution (Zippette dispenser) and shake well. Using a pipette add 50.0 ml of N/20 potassium thiocyanate solution. Using the 2.5 ml Zippette containing N/20 potassium thiocyanate solution, add single 2.5 ml "shots" from the Zippette swirling the contents of the flask until the first permanent red color is seen in the solution. Note the number of "shots" of thiocyanate added.

6. Transfer 50 ml of the *blank* solution to a conical flask. Add 10 ml (pipetted) of silver nitrate solution, 10 ml 50 percent nitric acid solution (Zippette), 2 ml nitrobenzene (Zippette) and 5 ml ferric alum solution (Zippette). Shake well. Titrate by *burette*, using approximate N/20 potassium thiocyanate solution, to the first permanent red color.

The blank is calculated as follows:

x = titre (ml); 100-x = back titre = y'; $\frac{y'}{2.5}$ = no. of thiocyanate shots equivalent to the chloride in the blank.

The number of thiocyanate shots equivalent to the blank chloride is *added* to the number of thiocyanate shots for the sample solution and the sum is used for the calculation of the percent by weight of water in the concrete as follows:

Let y = number of shots of KCNS + 20

then percent water in wet mix = $\frac{50\ y}{200-y}$

7. At regular intervals check the accuracy of the determination by analyzing a sample of wet concrete containing a known amount of water. Note that it is important to use oven-dry aggregate in the preparation of the test mix. If the recovery is less than 95 percent or more than 105 percent a systematic check of each stage of the analytical process will be necessary.

CEMENT CONTENT BY THE RAPID ANALYSIS MACHINE

by

J. A. Forrester

Cement and Concrete Association, England

Presented at CERL Conference on
RAPID TESTING OF FRESH CONCRETE
Champaign, Illinois
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ABSTRACT

Following an assessment of the requirements of the construction industry, a mechanized apparatus to measure the cement content of fresh concrete has been devised. This report describes the apparatus, its operation and testing. The sequence of procedure built into the apparatus starts with the elutriation of a weighed sample of concrete with water, whereby cement and other fine particles are separated as a slurry. This is followed by sub-sampling, flocculation and measurement of the cement by weight in a constant volume vessel. The process takes five minutes and is controlled by a preset sequence timer. Details of the functions involved are given and their effect on overall precision and accuracy are discussed.

In the absence of silt (i.e. aggregate of cement fineness), it is shown that the cement content of an 8 kg sample of concrete can be measured with a standard deviation of 21 g. A simple procedure for dealing with concretes containing appreciable amounts of silt is described; when this procedure is adopted, the standard deviation increases to 31 g.

Future developments are outlined. These include analysis of fresh concrete for water content, aggregate grading and possibly pulverized-fuel ash content.

CEMENT CONTENT BY THE RAPID ANALYSIS MACHINE

by

J. A. Forrester

INTRODUCTION

The quality of concrete is tacitly accepted when it is placed in a structure, and its cost in terms of the cost of its replacement increases rapidly with time from placement. This increase in cost, which is demcnstrated when there is a fault in the concrete quality, arises from the inevitable delay and disorganization of construction, the discussion and attempts at reappraisal which may involve additional testing, and the increasing difficulty of replacement. It is therefore obvious that rapid assessment of concrete quality can provide data for immediate engineering decision on the fate of the concrete and effect savings in costs.

A good contractor will design his target mix to be richer in cement than that specified so that the rate of failure to meet the specification, due to inherent fluctuations in batching, comes within the specified code of practice. To do this he must be aware of the fluctuation in quality from batch to batch. With an alternating variability arising from drift and correction the amplitude of variation will decrease if the time from preparing to testing is reduced. A reduced amplitude of variation will enable the contractor to design his target mix closer to that specified, while maintaining compliance with the code of practice. A savings in cement will then be made.

If it can be shown that analysis of fresh concrete is as good an assessor of concrete quality as concrete cube testing, then the increase in speed of obtaining results from analysis can bring economic advantages. With cements, aggregates, and water complying with required standards, only the proportions remain to be examined to ensure that the concrete quality is as good as the designed mix. With this done the responsibility for the concrete in the structure passes to the placer and compactor. Testing of these operations is best performed nondestructively.

With these aspects of acceptance, control, and compliance in mind the following design parameters for a machine to analyze concrete were

conceived. From an assessment made of the industry's needs[1] priority was given to measuring cement content, though consistency with further developments to make a module for measuring water content was considered. An operation time of 10 minutes to produce a result was set as a reasonable limit for acceptance criteria, and ease of operation was thought necessary to remove the influence of operator skill and fatigue. To be suitable for site the machine had to be self-cleaning, self-contained, and robust.

The level of precision to which the machine would operate had to be comparable to that obtained by concrete cubes and a precision of 5 percent of the cement content at the 95 percent confidence level was the target. It was also considered that the size of the sample analyzed should be that stipulated in BS 1881 pt 1; i.e., 5 kg for concrete with 25 mm maximum size aggregate and 10 kg for concrete with aggregate larger than 25 mm.

THE RAPID ANALYSIS MACHINE (R.A.M.)

A detailed description of the R.A.M. and its development is given in a report by Forrester, Black and Lees;[2] what follows is an abridgement and updating of that information.

The machine (Figure 1) is a floor-mounted portable unit having overall dimensions of 975 x 730 mm in plan X 1380 mm high and weighing 159 kg. It requires a water supply for continual use and either 110 or 230 volt single phase electrical supply either from the mains or from a portable generator. The component parts of the machine can be seen in Figure 2. A concrete sample of between 5 and 8 kg is taken, weighed and loaded via a hopper into the elutriation column of the machine. Water is pumped up the column from a reservoir tank; the concrete is unscrambled at the conical base and material of around 200 μm is lifted off as a slurry.

At the top of the column is a sampling head where one-tenth of the slurry is directed through a vibrating 150 μm sieve into a conical conditioning vessel where it is stirred and dosed with a flocculating agent. The base of the conditioning vessel is a detachable collecting pot into which the solids settle after stirring is finished. The rest of the slurry is sent to waste.

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[1] Heard, T. J. and Simmonds, W. H., *An Appraisal of the Requirements for the Rapid Analysis of Fresh Concrete and the Benefits of Adoption*, SIRA Report R474 (SIRA Institute, Chislehurst, Great Britain, August 1970).

[2] Forrester, J. A. and Black, P. F. and Lees, T. P., *An Apparatus for the Rapid Analysis of Fresh Concrete to Determine Its Cement Content*, Technical Report 42.490 (Cement and Concrete Association, April 1974).

The supernatant liquid is removed by controlled syphon tubes which pass into the conditioning vessel and terminate within the volume of the collection pot. One syphon tube is large, and removes liquid quickly; the other is smaller and removes liquid slowly and, by virtue of its length, separates after the coarse syphon has broken. The result is that the removable collection pot contains a fixed volume of solid and liquid whose weight is proportional to the weight of solid it contains. With each machine a calibration graph is prepared relating pot weight to weight of material of cement fineness in the original sample.

The whole operation, which takes place between the time of loading the concrete into the machine and the time the collection pot is removed, is controlled by a process timer and is completed within 5 minutes. After loading the machine, the operator has only to press a button which initiates the process timer, and then remove and weigh the collection pot. A dump valve at the base of the elutriation column enables the machine to be made ready for reuse in less than 5 minutes.

Some concretes are made with aggregates that contain a fraction that will pass a 150 μm sieve. With these concretes the calibration graph will indicate a higher cement content than the real value. If the amount of this material is small, say less than 2 percent, then it can easily be allowed for in a correction to the weight of cement derived from the calibration graph.

At such a level, the variation from sample to sample will be small. Where the silt content is higher, however, the variation from sample to sample can be large and appreciably affect the result. It has been found that although the silt content may vary widely as a fraction of the total aggregate, it will stay well within 10 percent of a fraction of the total aggregate which is elutriated. Therefore, if this fraction is found for any aggregate which contains a high silt content, the amount of silt mixed with the cement can be estimated from the weight of material held on the 150 μm sieve.

This material can be weighed in the collecting pot in a way similar to the cement-silt mixture. After constructing a simple correction line to the calibration curve, the weight of cement in the concrete can be derived from the weights of the collecting pot when it contains cement, silt, and water, and its weight when it contains sand and water.

The only admixtures found to affect the calibration are air entrainers. When air-entrained concrete is being analyzed, a small quantity of tributylphosphate must be mixed with the concrete before it is added to the elutriator. This successfully detrains any air in the subsequent flocculate.

If the aggregate grading is required, then the material removed from the elutriation column is wet-sieved and the fractions are

measured in a syphon can. The fine fraction obtained this way must be added to that which is retained on the 150 μm sieve and any silt that has passed with the cement through the sieve after these values have been corrected for the sampling head factor.

The apparatus is now being manufactured on a commercial scale, and is obtainable from the Development Unit of the Cement and Concrete Association, Great Britain.

Laboratory tests with a wide range of aggregates and mix proportions show that the cement content of concrete is measured with a constant standard deviation irrespective of the cement content. The results show that in the absence of silt there is 95 percent confidence of measuring the cement content to within ± 42.2g of the true value. In the presence of silt the error is ± 62g at the 95 percent confidence level. For a concrete with a bulk density of 2400 kg these values represent ± 12.7 and ± 18.7 kg of cement per cubic meter, respectively.

One independent evaluation of the rapid analysis machine[3] concludes from the results of using the machine on concretes with a variety of cements, aggregates, water/cement ratios and admixtures that the accuracy of the machine is ± 5.5 percent at the 99.9 percent confidence level.

A rapid analysis machine was mounted in a mobile laboratory, together with a 240 volt, 3.5 KVA portable generator, and taken to 16 construction sites around England. The purpose was to demonstrate the utility of the machine and to test its performance with a wide variety of concretes and aggregates. Wherever site concrete was analyzed, sufficient concrete was taken to perform duplicate analyses and this enabled the results to be analyzed. In all, 110 batches of concrete were analyzed in duplicate and from a consideration of these results the estimated standard deviation for a single sample was ± 35 g of cement corresponding to ± 21 kg of cement per cubic metre of concrete that has a bulk density of 2400 kg/m^3 at the 95 percent confidence level. This value, which includes an undetermined but small subsampling error, introduced by duplication, compares well with that obtained during laboratory trials.

On some sites it was possible in the time available to monitor a number of consecutive but notionally identical batches of concrete and subsequently to compare the results of analysis with 28-day-old site cubes. Figures 3 and 4 show two examples of correlation of strength and cement content.

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[3] Hutchinson, N., *Rapid Analysis of Cement Content in Fresh Concrete*, Report 014J/74/1676 (Taylor Woodrow Construction Research Laboratories).

CONCLUSION

The rapid analysis machine has been tested in the laboratory and on many sites. It has analyzed a wide variety of concretes containing different aggregate type and silt contents. The precision found on site differs very little from that found in the laboratory.

In-laboratory precision at the 95 percent confidence level expressed on a concrete whose bulk density is 2400 kg/m^3 is ± 19 kg/m^3 for a single determination and on-site precision was found to be ± 21 kg/m^3 at the same level. An analysis can be completed within 10 minutes and the apparatus made ready for reuse in another 5 minutes.

ACKNOWLEDGEMENTS

The author acknowledges the help of Mr. T. P. Lees and Mr. J. Figg in performing the analyses in the laboratory and on site.

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Hutchinson, N. *Rapid Analysis of Cement Content in Fresh Concrete* Report 014J/74/1676 (Taylor Woodrow Construction Research Laboratories).

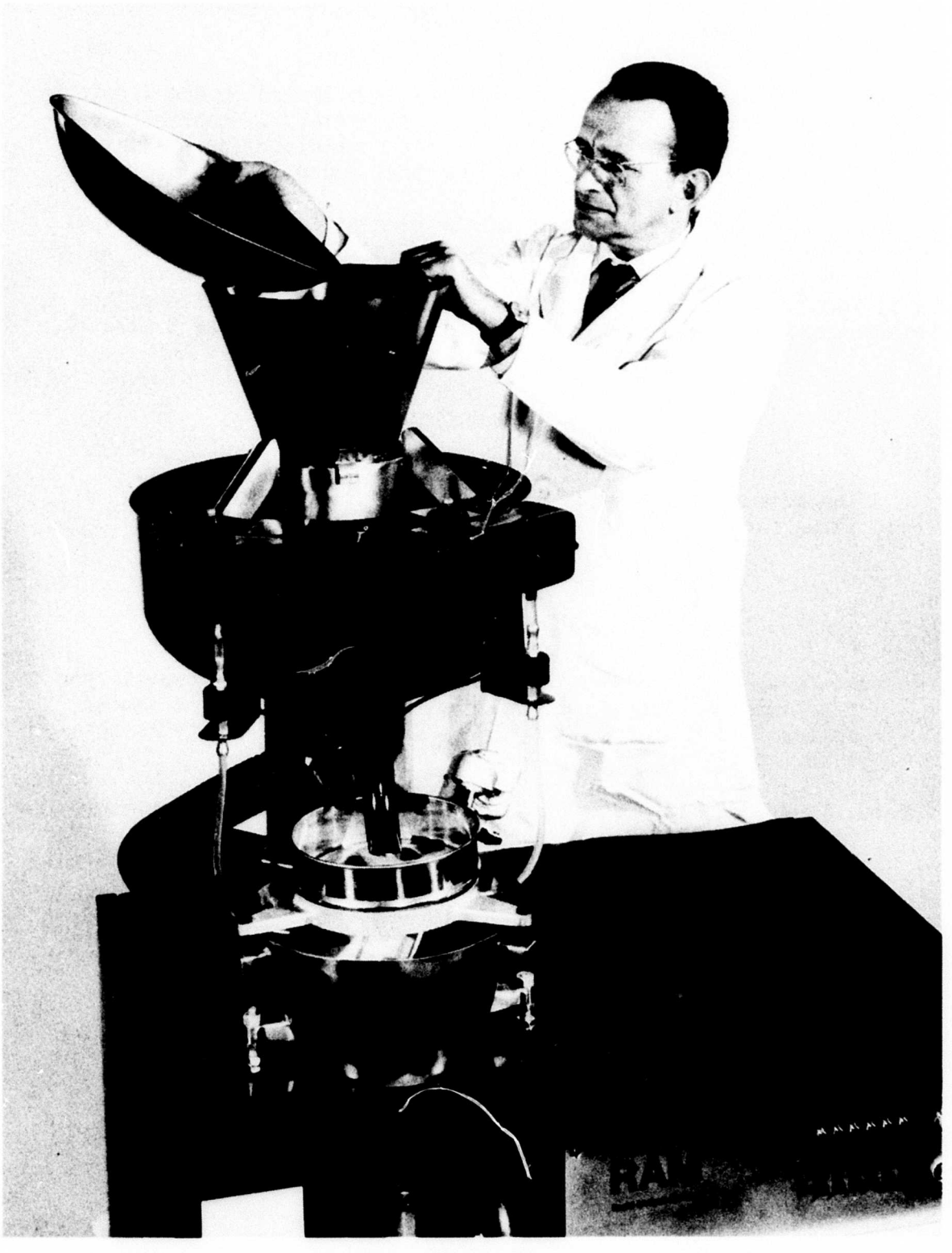

Figure 1. Rapid Analysis Machine.

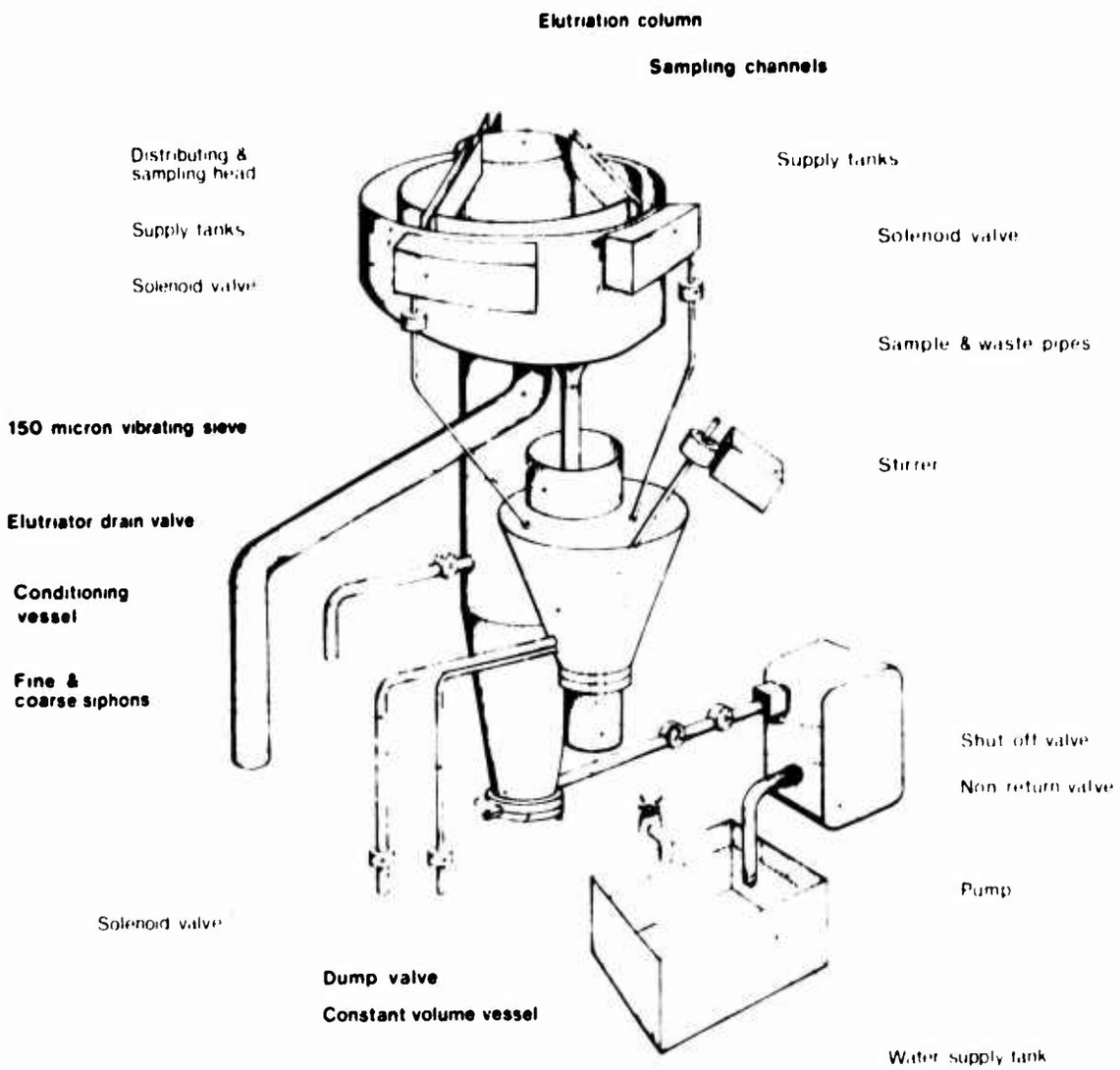

Figure 2. Component parts of RAM.

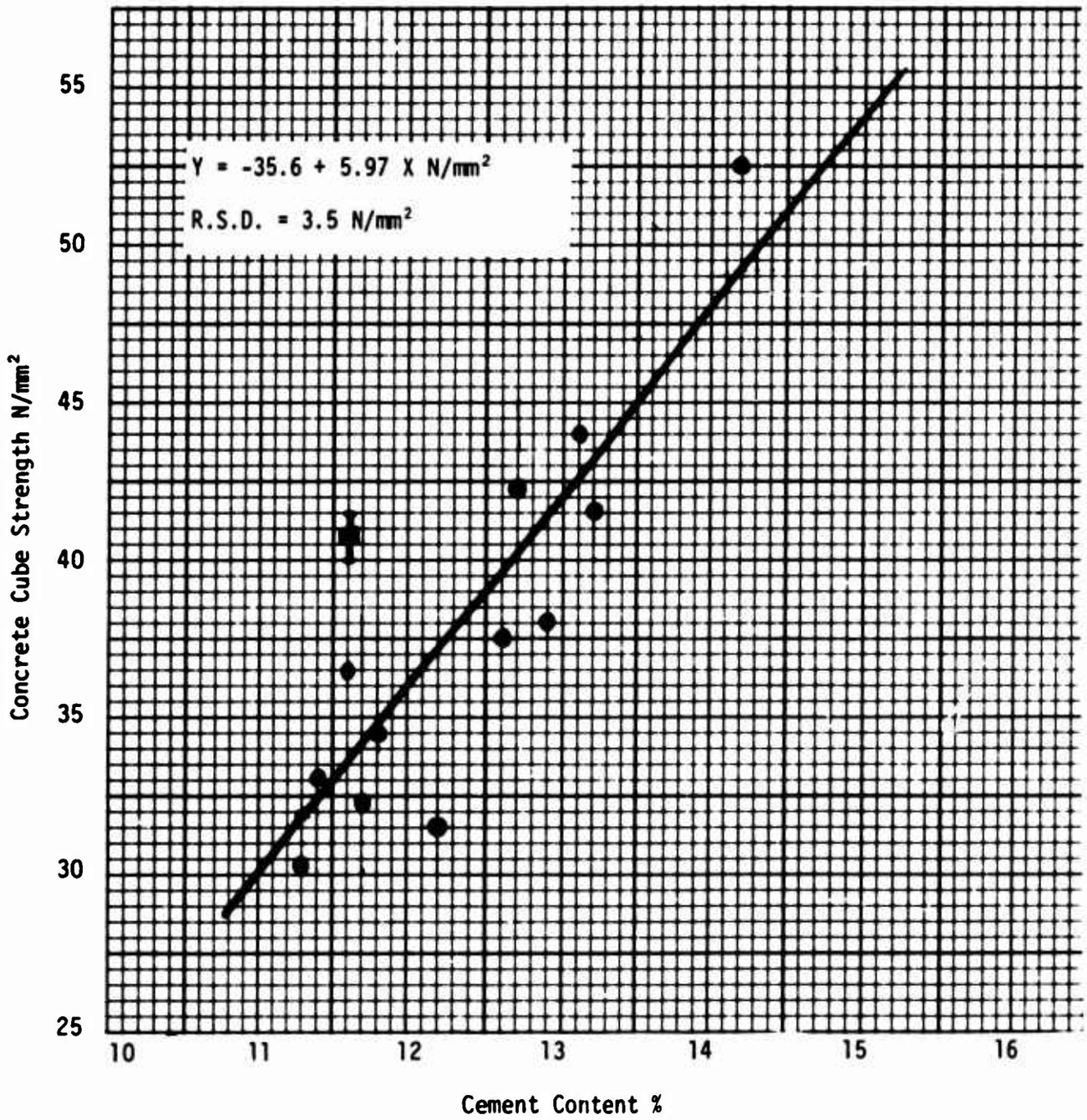

Figure 3. Correlation of strength with cement content Solihull Car Factory.

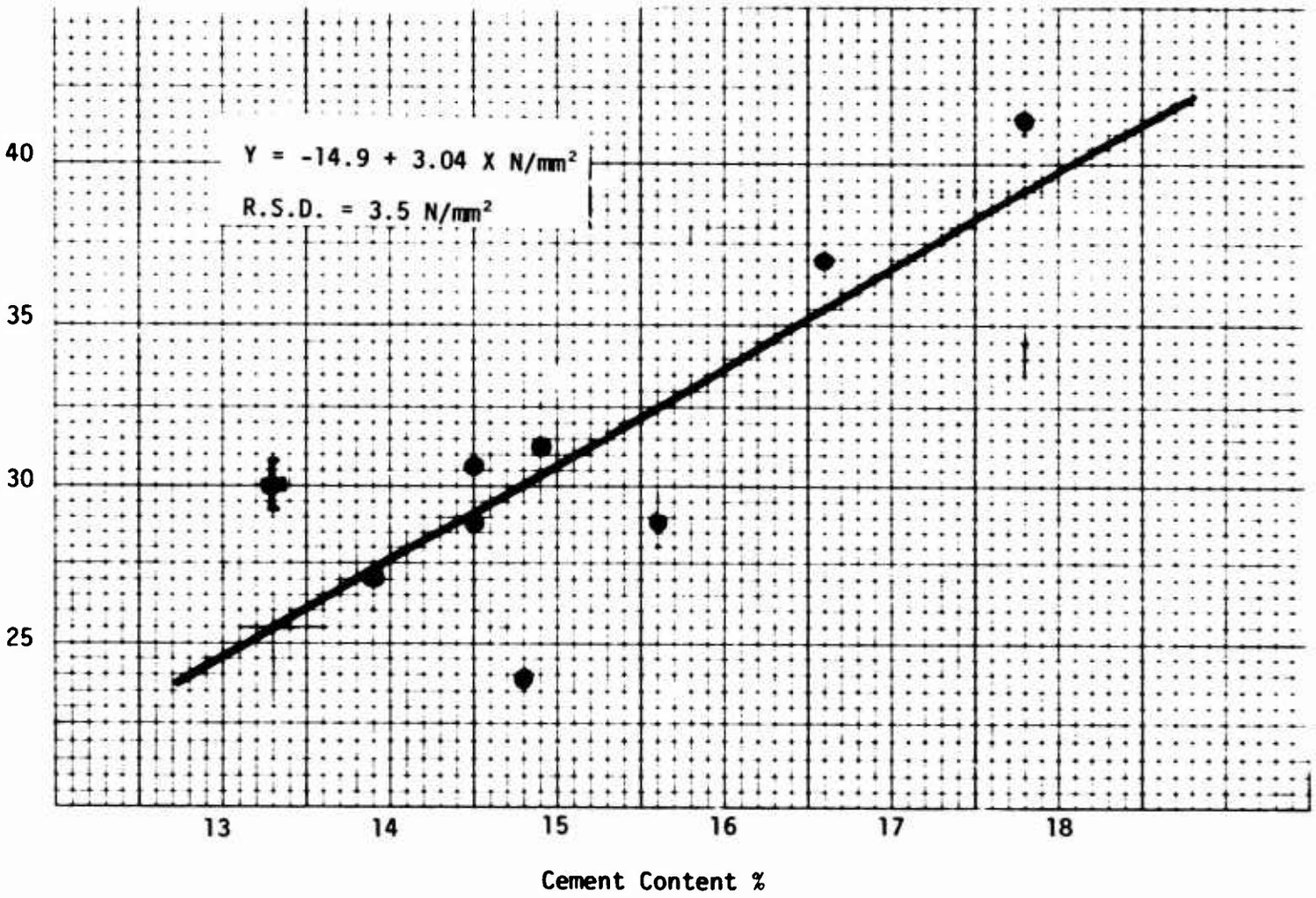

Figure 4. Correlation of strength with cement content Devonport Dockyard.

CORRELATING KELLY-VAIL TEST RESULTS TO THE STRENGTH POTENTIAL OF FRESH CONCRETE

by

Paul A. Howdyshell

Civil Engineer
Construction Engineering Research Laboratory

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ABSTRACT

This paper discusses the influence of water and cement content on concrete strength and develops a mathematical model relating the measurement errors for determining water and cement content to the reliability in computing compressive strength. The paper presents experimental data from the Kelly-Vail study relating water and cement content to 28-day compressive strength.

Test results indicate that the Kelly-Vail method for determining water and cement content can be used to predict the potential strength of fresh concrete. The reliability of predicting strength by this procedure is equal to that of predicting strength based on actual mix proportions. For the normal range of aggregate type and size and a given cement type, air entrainment appears to be the only other material parameter that significantly influences strength. Thus, when the Kelly-Vail system is used in conjunction with an air content test, there is a rapid means (approximately 15 min.) for determining potential concrete strength.

CORRELATING KELLY-VAIL TEST RESULTS TO THE STRENGTH POTENTIAL OF FRESH CONCRETE

by

P. A. Howdyshell

INTRODUCTION

It is acknowledged that current procedures for evaluating the quality of concrete are deficient; however, it is also acknowledged that if new methods are to gain general acceptance, they must be related to present standard procedures. When evaluating methods to determine the water and cement content of fresh concrete, it is desirable to determine whether water and cement content test results can be correlated to standard 28-day compressive strengths.

This paper discusses the influence of water and cement content on concrete strength and develops a mathematical model relating the measurement errors in determining water and cement content to the reliability in computing compressive strength. It presents experimental data from the Kelly-Vail study relating water and cement content to 28-day compressive strength.

WATER/CEMENT RATIO VS CONCRETE STRENGTH

It is generally accepted that the water/cement ratio of a specific type of concrete is the primary parameter influencing its potential strength. Proper consolidation and curing must occur if the fresh concrete is to reach its maximum potential strength. In addition, such parameters as maximum aggregate size, aggregate shape and surface texture, aggregate gradation, and air entrainment influence the concrete's potential strength; however, within aggregate and air content variations allowed in normal concrete, their influences are secondary when compared with that of the water/cement ratio.

There have been many attempts to model the influence of water/cement ratio on concrete strength. Lorman listed 10 equations that have been developed which relate 28-day compressive strength to water/cement ratio,[1]

[1] W. R. Lorman, "Verifying the Quality of Freshly Mixed Concrete," *Proceedings of the American Society of Testing and Materials*, Vol 62 (1962), pp 952-955.

but probably the most extensive work in the area was conducted by Powers of the Portland Cement Association.[2]

Powers' "gel space ratio" is the most widely accepted strength equation, even though it neglects aggregate influence on concrete strength. Parameters included in the equation are the water/cement ratio and the degree of hydration. The gel space ratio, (X), is:

$$X = \frac{0.647\alpha}{.319 + W_o/C} \qquad \text{[Eq 1]}$$

where α = fraction of cement hydrated
C = weight of cement
W_o = weight of water

Powers experimentally determined that the relation between compressive strength (f_c) of 2-in. mortar cubes and the gel space ratio is:

$$f_c = 34X^3 \text{ Kip.in.}^2 \qquad \text{[Eq 2]}$$

ERROR ANALYSIS MODEL, WATER/CEMENT RATIO VS STRENGTH

Standard error analysis techniques are used to model the relation between errors in measuring water and cement content and compute variations in concrete strength. Appendix A contains the development of the error analysis model for strength, which is based on Powers' gel space ratio equation (Equations 1 and 2).

The relation between measured errors in determining water and cement content and the computed error in predicting strength is (Appendix A):

$$\sigma_{f_c}^2 = \left[\left(\frac{W}{C}\right) \frac{8.2}{C\left(.242 + \frac{W}{C}\right)^4}\right]^2 \sigma_c^2 + \left[\frac{-8.2}{C\left(.242 + \frac{W}{C}\right)^4}\right]^2 \sigma_w^2 \qquad \text{[Eq 3]*}$$

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[2] T. C. Powers, "The Physical Structure and Engineering Properties of Concrete," *Research Department Bulletin 90* (P.C.A., July 1958).

* Equation 3 is based on 76 percent hydration, which is approximately equal to a 28-day moist cure and $f_c = 22.95X^3$.

where σ_{f_c} = standard deviation-compressive strength

σ_c = standard deviation-cement content

σ_w = standard deviation-water content

C = weight of cement

W = weight of water

Figure 1 is a graphical representation of the relation between the coefficient of variation (c.v.) for water and cement and the computed c.v. for strength, based on a water/cement ratio of .578, 76 percent hydration, and an aggregate/cement ratio of 5:1. For these given values, a reasonable approximation of the relationship between water and cement c.v., (assuming water c.v. = cement c.v.) and the computed c.v. strength is:

$$(c.v.)_{f_c} = 2.86\ (c.v.)_W \qquad [Eq\ 4]$$
$$= 2.86\ (c.v.)_C$$

Thus, if the c.v. for measuring water and cement content is 5 percent, the strength potential of the mix can be computed with an expected accuracy of about 15 percent.

KELLY-VAIL TESTS VS COMPRESSIVE STRENGTH

To assess the Kelly-Vail water and cement content system, the Construction Engineering Research Laboratory (CERL) evaluated the feasibility of using the water and cement contents obtained from the Kelly-Vail test to estimate the 28-day compressive strength of concrete.

The Kelly-Vail laboratory evaluation included tests on: two aggregates (a sand and gravel, and a sand and crushed limestone); three aggregate sizes (a 3/8-in., 3/4-in., and 1 1/2-in. maximum aggregate); two types of cement (Type I and Type III portland cements); one pozzolanic material (flyash); three levels of air entrainment (approximately no air, 3 percent, and 6 percent); and three mix designs (3000, 4500, and 6000 psi concrete). Seventy batches of concrete were tested during the laboratory evaluation.

Test Procedure

The tests included the following procedures:

1. Weighing out the mix ingredients for a 2 or 2 1/2 cu ft mix, and obtaining representative aggregate samples for moisture determination.

2. Mixing the concrete for 5 min in a 3 1/2 cu ft capacity drum mixer. (Six mixes ran for 45 minutes.)

3. Taking one 10-lb sample for the Kelly-Vail water-cement analysis, running a slump and air content test, and casting six 6 x 12 in. cylinders.

4. Obtaining a second 10-lb sample for Kelly-Vail water and cement analysis.

A complete standard Kelly-Vail water and cement analysis was run on both samples. (Appendix B describes the Kelly-Vail test procedure.)

The companion cylinders were moist cured; three were broken after 7 days, and three were broken after 28 days.

Analysis and Discussion of Tests Results

Data obtained from the Kelly-Vail tests were analyzed to determine their overall accuracy and to determine if the procedure can be used to estimate concrete strength potential. Percent recovery (measured values divided by actual values) was the basis for evaluating overall accuracy.

Table 1 indicates that for all samples, the average recovery for cement was 94.6 percent, and free water 94.8 percent. The related coefficients of variation were cement--7.9 percent, and free water--6.2 percent. Table 1 also contains water and cement recovery and error values for the tests grouped by cement type, aggregate type, and aggregate size.

Contrary to information presented in an interim report,[3] the complete laboratory study indicates that sub-grouping by aggregate type does not reduce error magnitude. Due to inconsistencies in the subgroup sizes and the small number of samples, it is difficult to determine whether the large coefficient of variation for the Type III cement or the small coefficient of variation for the 3/8 in. aggregate are meaningful. With the exception of these two subgroups, the coefficients of variation for the other subgroups are very similar to the overall values of 7.9 and 6.2 percent, respectively, for cement and water.

[3] P. A. Howdyshell, *Laboratory Evaluation of a Chemical Technique to Determine Water and Cement Content of Fresh Concrete*, Technical Report M-97 (Construction Engineering Research Laboratory [CERL], July 1974).

Table 1

Recovery and Error in Determining Water and Cement Content

GROUP		CEMENT			WATER (FREE)	
		No. of Samples	Average Recovery	Coefficient of Variation	Average Recovery	Coefficient of Variation
All Samples		70	94.6	7.9	94.8	6.2
Cement Type	Type I	58	94.1	6.5	95.0	6.4
	Type III	12	97.1	12.6	93.9	5.7
Aggregate Type	Gravel	35	95.5	8.0	95.5	5.4
	Limestone	35	93.7	7.8	94.1	7.0
Maximum Aggregate Size	3/8 in.	6	97.4	2.4	89.9	3.3
	3/4 in.	58	95.2	8.0	96.3	5.9
	1 1/2 in.	6	89.6	9.3	93.9	6.9

To evaluate whether the Kelly-Vail water and cement contents could be used to estimate concrete strength potential, regression analysis curves (with 80 percent confidence bands) were developed relating 28-day compressive strength to both Kelly-Vail and actual water/cement ratios, and to Kelly-Vail water/cement ratios versus actual water/cement ratios.* The water/cement ratio strength curves were developed for subgroups such as cement type, aggregate type and size, air entrainment, etc. (see Table 2). Figures 2, 3, and 4, respectively, represent Kelly-Vail water/cement ratios versus 28-day compressive strength; actual water/-cement ratios versus 28-day compressive strength; and the Kelly-Vail versus actual water/cement ratios for the Type I cement, non-air-entrained concretes. When the 80 percent confidence bands of Figures 2 and 3 are compared, it is noted that the confidence bands for predicting strength from the Kelly-Vail results are slightly smaller (775 versus 900 psi) than the confidence bands for the actual water/cement ratios. Table 2 similarly compares the various subgroups. Most subgroups produced confidence bands similar to these listed above, with the largest Kelly-Vail band being 1065 psi for the non-air-entrained Type III cement series.

When comparing the 80 percent confidence bands obtained from the regression analysis (Figure 2, Table 3) to the gel space ratio model (Eq 3, Figure 1), it is noted that the model predicts that the strength estimation error is a constant function of strength. The regression curves, however, indicate that the strength estimation error is constant over the range of strengths evaluated. Thus, a direct comparison of the two is difficult. For some nominal strength value, for example 5000 psi, the 80 percent confidence band for the model would be $\pm$ 1250 psi as compared to $\pm$ 775 psi (Table 2) for the regression analysis (based on 6.2 and 7.9 percent coefficient of variation for water and cement content, respectively, Figure 1 indicates that the strength coefficient of variation equals 20 percent and that the 80 percent confidence equals 1.28 standard deviations). Thus for most cases, the model predicts greater sensitivity to the measurement errors than what actually occurred in the regression analysis.

The data indicated that the Kelly-Vail procedure can predict strength potential with an error no greater than if strength determination is based on actual water/cement ratios of the mixes. However, the level and frequency of calibration required to relate Kelly-Vail water and cement contents to 28-day strengths must be evaluated. For this purpose, regression analysis curves relating Kelly-Vail water/cement ratios to 28-day compressive strengths for various subgroups are compared. Figures 5 and 6 indicate that aggregate type and aggregate size within those limits found in normal concrete do not significantly alter the strength-

* Actual water content is based on free water available, assuming the aggregate becomes saturated, and is determined by knowing the quantity of mix water modified by the moisture content of the aggregate for each concrete batch.

Table 2

Reliability for Estimating Strength Potential from Actual and Kelly-Vail Determined Water/Cement Ratios

Group	Subgroup Evaluated	Actual psi	K-V psi	Error in Predicting Actual from K-V Water/Cement Ratios
Type I Cement No Air, 3/8, 3/4, 1-1/2 Max. Agg. Gravel & Limestone		±900	±775	±.065
Type I Cement No Air, 3/8, 3/4, 1-1/2 Max. Agg. Gravel	Agg. Type	±860	±785	±.065
Type I Cement No Air, 3/8, 3/4, 1-1/2 Max. Agg. Limestone	Agg. Type	±850	±630	±.064
Type I Cement No Air, 3/8 Max. Agg. Gravel & Limestone	Agg. Size	±410	±450	±.029
Type I Cement No Air, 3/4 Max. Agg. Gravel & Limestone	Agg. Size	±690	±730	±.064

Table 2 (cont'd)

Group	Subgroup Evaluated	Actual psi	K-V psi	Error in Predicting Actual from K-V Water/Cement Ratios
Type I Cement No Air, 1-1/2 Max. Agg. Gravel & Limestone	Agg. Size	±570	±950	±.086
Type I Cement 3/8 Oz. Air Ent. Agent 3/4 Max. Agg. Gravel & Limestone	Air Content	±215	±385	±.038
Type I Cement 3/4 Oz. Air Ent. Agent 3/4 Max. Agg. Gravel & Limestone	Air Content		±400	±.036
Type I Cement + 25% Flyash, No Air 3/4 Max. Agg., Gravel & Limestone	Pozzolan	±460[1]	±800[1]	±.065[1]
Type I Cement + 25% Flyash, No Air, 3/4 Max. Agg., Gravel & Limestone	Pozzolan	±475[2]	±810[2]	±.050[2]
Type III Cement No Air 3/4 Max. Agg. Gravel & Limestone	Cement Type	±530	±1065	±.125
Type III Cement 3/4 Oz. Air Ent. Agent 3/4 Max. Agg. Gravel & Limestone	Cement Type	±420	±360	±.065

NOTE: [1]Water/cement ratios based on cement only
[2]Water/cement ratios based on cement plus flyash

water/cement ratio relationship.

Figures 7, 8, and 9 indicate that air entrainment, cement type, and substituting pozzolanic materials for cement are three parameters that alter the strength-water/cement ratio relationship enough to require development of new curves. Of the three, cement type and pozzolanic materials do no significantly alter the ratio. There are only five cement types (three of which are usually available); pozzolanas are used rarely (normally in mass concrete where development of new calibration curves would be economically feasible).

Air entrainment causes a problem by affecting concrete strength. Air entrainment is a very common admixture used in most concrete subjected to a freeze-thaw environment, and its influence depends on the amount of air entrained. This requires a family of curves to be generated over the range of air contents normally encountered. Figure 10 is a regression analysis model relating Kelly-Vail water/cement ratios to strength over a range of air contents varying from .5 percent to 7 percent.

CONCLUSION

The laboratory evaluation of the Kelly-Vail procedure has indicated that the results can be used to predict a concrete's potential strength. The reliability of predicting strength by this procedure is equal to that of predicting strength by a procedure based on actual mix proportions. Furthermore, the measurement error for determining the amount of water and cement has a smaller effect on predicting actual strength than is indicated by the gel space ratio model. Air entrainment appears to be the only other major concrete material parameter that influences strength of cement having a normal range of aggregate type and size. Thus, if a concrete's air, cement, and water contents are measured, the material's potential strength can be predicted. The Kelly-Vail test, when used in conjunction with a device to measure air entrainment provides a rapid means (approximately 15 minutes) for determining the potential strength of fresh concrete. By using such a system, field personnel could perform time quality control on concrete prior to placement of the material.

APPENDIX A:
ERROR ANALYSIS - MEASURED VALUES VS COMPUTED PARAMETERS

If the errors associated with measured parameters are expressed in terms of standard deviation units, the functional relationship between calculated error and measured errors can be expressed as:

$$\sigma_t^2 = A_x^2 \ \sigma_x^2 + A_y^2 \ \sigma_y^2 \qquad \text{[Eq 1a]}$$

where t = calculated value

x, y = observed variables

$A_x = \frac{\partial t}{\partial x}$; $A_y = \frac{\partial t}{\partial y}$

σ = standard deviation of subscript.

For the gel space ratio equation:

$$fc = 22.95\left(\frac{0.647a}{0.319a + w/c}\right)^3 \qquad \text{[Eq 2a]}$$

assuming a = .76

$$fc = 22.95\left[\frac{.492}{.242. + w/c}\right] = \frac{2.733}{(.242 + w/c)^3} \qquad \text{[Eq 3a]}$$

$$\frac{\partial fc}{\partial w} = \frac{-8.2}{c(.242 + w/c)^4} \qquad \text{[Eq 4a]}$$

$$\frac{\partial fc}{\partial c} = \frac{8.2w}{c^2(.242 + w/c)^4} \qquad \text{[Eq 5a]}$$

and

$$\sigma_{fc}^2 = \left[\frac{8.2w}{c^2(.242 + w/c)^4}\right]^2 \sigma_c^2 + \left[\frac{-8.2}{c(.242 + w/c)^4}\right]^2 \sigma_w^2 \qquad \text{[Eq 6a]}$$

APPENDIX B:
THE ANALYSIS OF FRESH CONCRETE--SITE METHOD AND EQUIPMENT*

Method for Determining Water Content

Required Reagents

1. Nitrobenzene

2. Ferric alum solution (saturated)

3. Silver nitrate solution, approximately N/2 in distilled water

4. Sodium chloride solution, approximately N/2 in tap water

5. Potassium thiocyanate solution, approximately N/20 in distilled water.

6. 50 percent nitric acid solution in tap water.

Adjust the final concentrations of solutions (3), (4), and (5) to the exact ratio of 1:1:10, respectively, and check by titration.

Apparatus

1. End-over-end universal lab mixer. Fitted with widemouthed polyethylene bottle of approximately 1/2 gal capacity.

2. Constant volume dispensers. One 10-ml, one 5-ml, one 2.5-ml, one 2-ml, two-50 ml, and one 10-ml automatic pipettes; one 100-ml burette; two 550-ml Erlenmeyer flasks; two 500-ml volumetric flasks; two 50-ml volumetric pipettes.

Procedure

1. Weigh two 1-kg samples of fresh concrete to the nearest gram. Place one sample in a widemouthed bottle, and add 500 ml of distilled water. Secure the lid on the bottle. This sample is the blank required for estimating chloride in the concrete.

2. Transfer the second 1-kg sample to another widemouthed bottle. Add 500 ml of the approximately N/2 sodium chloride solution, and secure the lid.

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* R. T. Kelly and J. W. Vail, "Rapid Analysis of Fresh Concrete," *Concrete* (April 1968), pp 140-145.

3. Secure the two bottles onto the end-over-end mixer, and mix for a minimum of 3 min.

4. Pipette 50 ml of the clear sample solution into the Erlenmeyer flask containing 50 ml (pipetted) of silver nitrate solution. Add 10 ml of 50 percent nitric acid solution from a constant volume (c.v.) dispenser, and mix. Add 2 ml of nitrobenzene (c.v. dispenser), and shake well to coat the silver chloride precipitate. Add 5 ml of ferric alum solution (c.v. dispenser), and shake well, Add (by pipette) 50.0 ml of N/20 potassium thiocyanate solution. Using the 2.5 ml c.v. dispenser containing N/20 potassium thiocyanate solution, add single 2.5 ml "shots" from the c.v. dispenser while swirling the contents of the flask. Stop when the first permanent red color appears in the solution, and note the number of "shots" of thiocyanate added.

5. Transfer 50 ml of the blank solution to an Erlenmeyer flask, and add 10 ml (pipetted) of silver nitrate solution, 10 ml of 50 percent nitric acid solution (c.v. dispenser), 2 ml of nitrobenzene (c.v. dispenser), and 5 ml of ferric alum solution (c.v. dispenser). Shake well. Titrate by burette, using approximately N/20 potassium thiocyanate solution, until the first permanent red color appears.

The blank is calculated as follows: x = titre (ml); 100-x = back titre = y´; ´y/2.5 = number of thiocyanate shots equivalent to the chloride in the blank.

The number of thiocyanate shots equivalent to the blank chloride is added to the number of thiocyanate shots for the sample solution. The sum is used to calculate the percent by weight of water in the concrete as follows: let y = number of shots of KCNS + 20; then the percent water in wet mix = 50y/200-y.

6. At regular intervals, check the accuracy of the determination by analyzing a sample of wet concrete containing a known amount of water. (It is important to use oven dry aggregate when preparing the test mix.) If the recovery is less than 95 percent or more than 105 percent, a systematic check of each stage of the analytical process will be necessary.

Method for Determining Cement Content

Reagents

1. Five percent nitric acid solution. Add 5 ml HNO_3 (specific gravity 1.42) to 95 ml tap water.

2. Tap water

3. Standard cement solution. Select a 1.50 gr sample of fresh cement. Add 50 ml tap water and 10 ml HNO_3 (s.g. 1.42). Stir the solution

until the cement has been completely dissolved. Make up to 1000 ml in a graduated flask with tap water, and mix well (must be used within 2 hours). With appropriate dilutions, this standard is used to prepare the calibration curve for the flame photometer.

4. Standard calcium solution. Place 1.60 gr of dried $CaCO_3$ in a 250-ml beaker, and cover with 100 ml tap water. Carefully add 10 ml HNO_3 (s.g. 1.42), and cover the beaker immediately. When this is dissolved, make up to 1700 ml with tap water.

This standard calcium solution should then be adjusted in strength until it gives a reading of 100 on the flame photometer when the instrument is set to read 100. (The setting is accomplished with a freshly prepared standard cement solution containing 1.50 gr cement/liter as described above.) Once adjusted, the calcium solution is used for the day-to-day checking of the flame photometer's maximum deflection setting.

Apparatus

1. Single-tub washing machine. Must have a smooth interior, side-mounted impeller, and a recirculating pump and hose. The recirculating hose should be fitted with a T-piece for connection to the automatic pipette. The working capacity of the tub must be 37.6 liters.

2. Linked pipette assembly. 125 ml for sampling cement suspension, 100 ml for nitric acid, and 300 ml for dilution water.

3. Domestic high speed mixer (milk shake type).

4. Flame photometer. Operating from oxygen and butane bottles.

5. Two 20-liter rectangular carboys containers for reagents.

Procedure

1. Fill the washing machine to the mark in the tank with 37.6 liters of tap water.

2. Charge the automatic pipettes with their appropriate reagents, i.e., 300 ml of tap water and 100 ml of 5 percent nitric acid solution.

3. Start the flame photometer in the following manner:

a. Make sure that both oxygen and butane supplies are off. (Turn the oxygen regulator counterclockwise until it moves freely.)

b. Ignite the flame by opening the butane valve. (Butane pressure should be approximately 1 1/2 in. of water and can be adjusted by needle valve.)

c. Apply oxygen by turning the regulator handle clockwise until the pressure reads 13 psi.

4. Mix the concrete sample to ensure homogeneity, and weigh out 1 kg of fresh concrete to the nearest gram.

5. Transfer the weighed concrete to the sieves placed over the washing machine. Switch on the washing machine, and wash the residue from the 1-kg sample container into the machine, with the jet of water from the recirculating pump hose.

6. Wash the +No. 4 aggregate carefully with the jet of water from the recirculating pump hose. After cleaning, remove the No. 4 sieve (should take about 1 1/2 min).

7. Wash the +No. 50 aggregate for about 1 1/2 min. Keep the jet of water moving slowly over the sieve's surface to avoid loss of the suspension by splashing.

8. Take an aliquot, using an automatic pipette (125 ml). (Place a finger over the larger bore of the T-piece on the end of the pump hose to direct the suspension into the automatic pipette. When the pipette is full, simultaneously remove finger and switch off the lower pipette tap.)

9. Run the 125-ml aliquot of the suspension into the mixer cup. Wash out the automatic pipette, using the 100 ml and 5 percent nitric acid solution contained in the automatic pipette fitted above the sample pipette. These washings also run into the mixer cup. Add 300 ml of tap water from the appropriate automatic pipette.

10. Fix the cup to the high speed stirrer, and stir for 3 min to ensure a complete solution of cement.

11. Use tap water to set zero, and standard calcium solution to set 100 (full scale) on the flame photometer. Record the photometer reading for the sample solution, flushing the instrument with distilled water between each reading. The reading for the sample solution is converted by the calibration curve previously prepared to a value A gr of cement/-liter of the final solution.

Percent cement in wet mix =

$$A \times \frac{\text{(volume of aliquot + acid + dilution water)}}{\text{volume of aliquot}} \times \frac{\text{volume of water in mixing tub}}{10{,}000}$$

12. At regular intervals, make sure that the equipment is operating satisfactorily by analyzing a sample of wet concrete containing a known amount of cement. If the recovery is less than 90 percent or more than 105 percent, each stage of the analytical process must be systematically checked.

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Kelly, R. T. and J. W. Vail, "Rapid Analysis of Fresh Concrete," *Concrete* (April 1968), pp 140-145.

Lorman, W. R., "Verifying the Quality of Freshly Mixed Concrete," *Proceedings of the American Society of Testing and Materials*, Vol 62 (1962), pp 952-955.

Powers, T. C., "The Physical Structure and Engineering Properties of Concrete," *Research Department Bulletin 90* (P. C. A., July 1958).

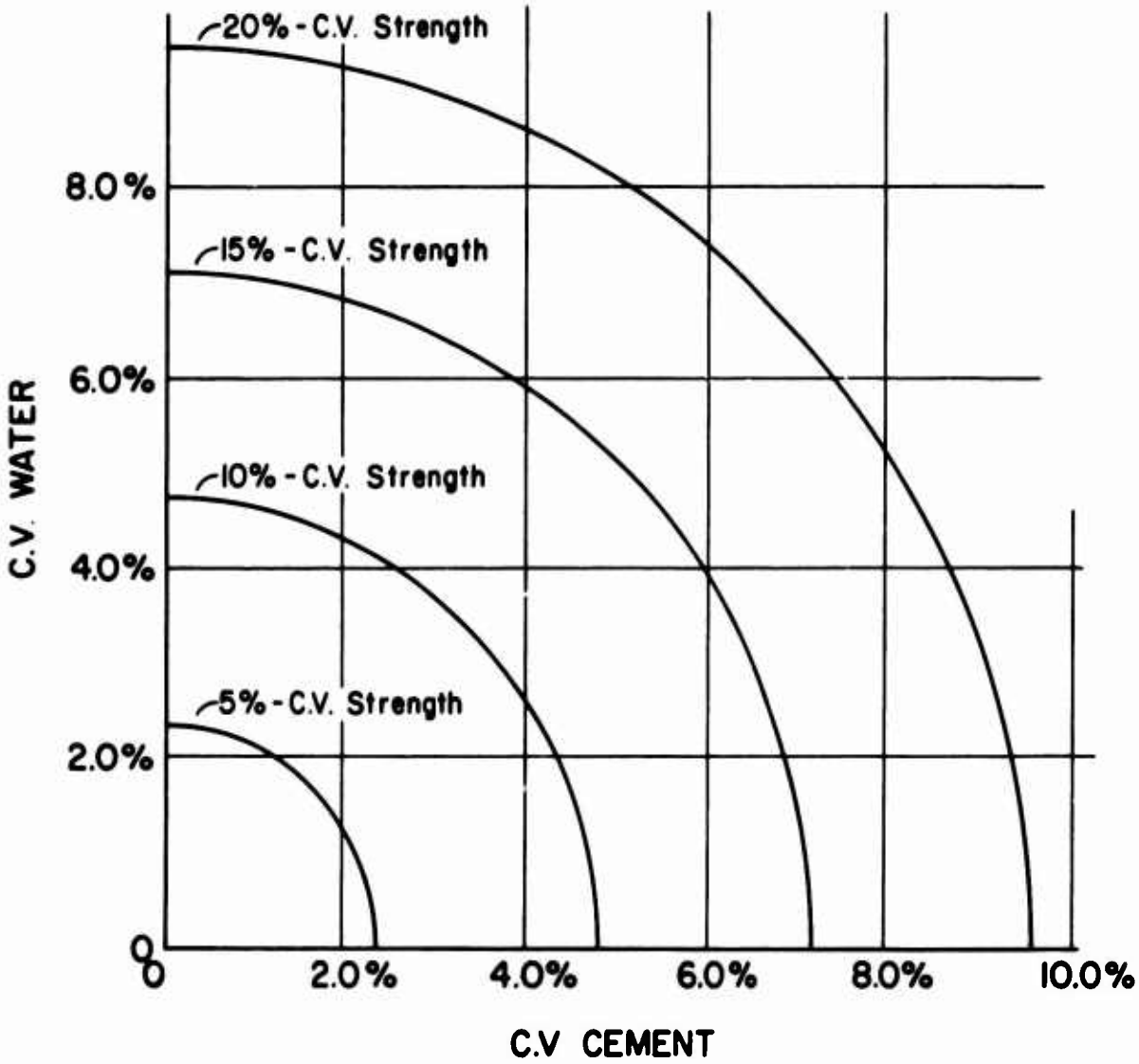

Figure 1. Error analysis model coefficients of variations (c.v.) for water and cement content vs. 28 day strength.

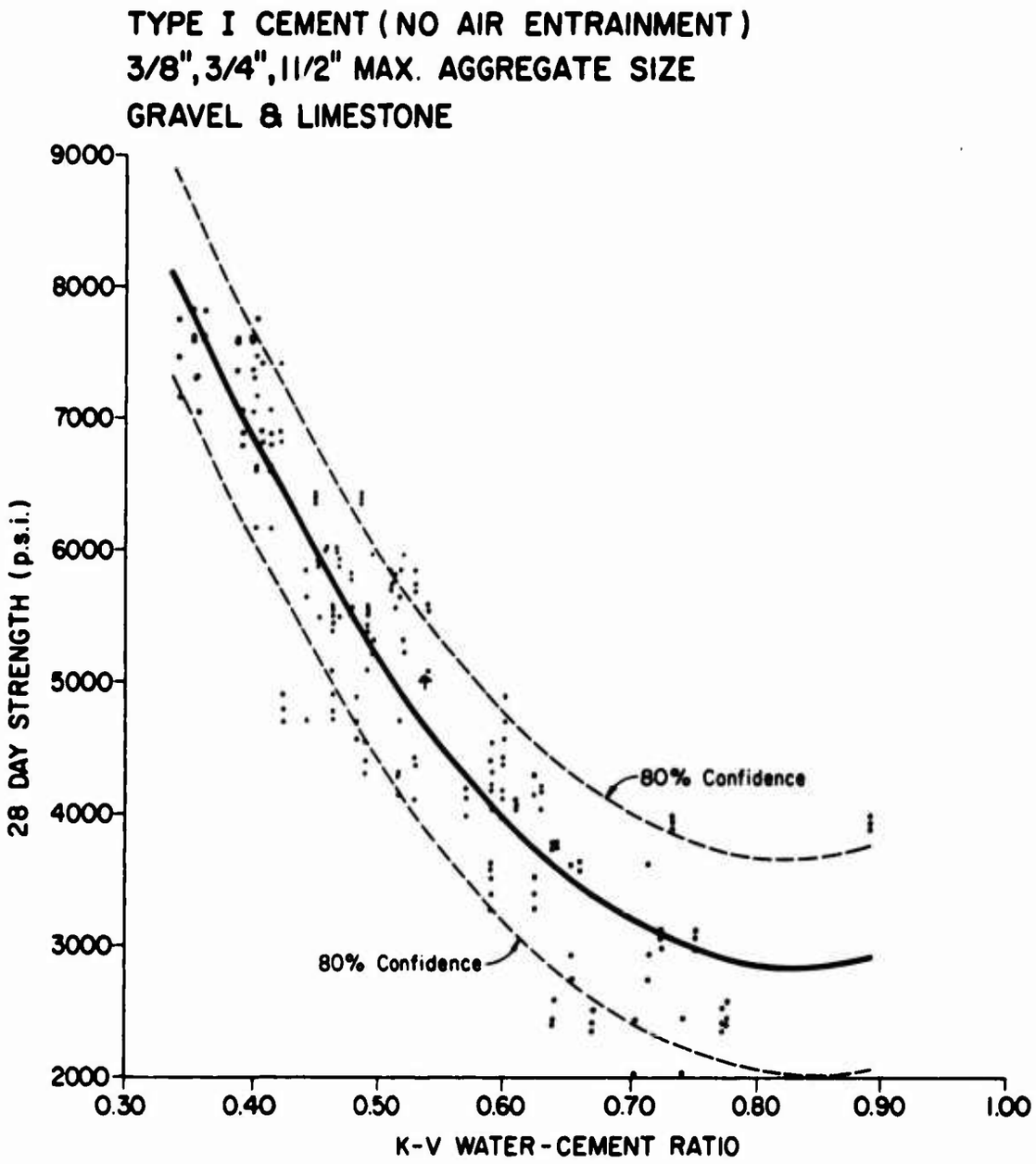

Figure 2. K-V water/cement ratio vs. 28 day compressive strength.

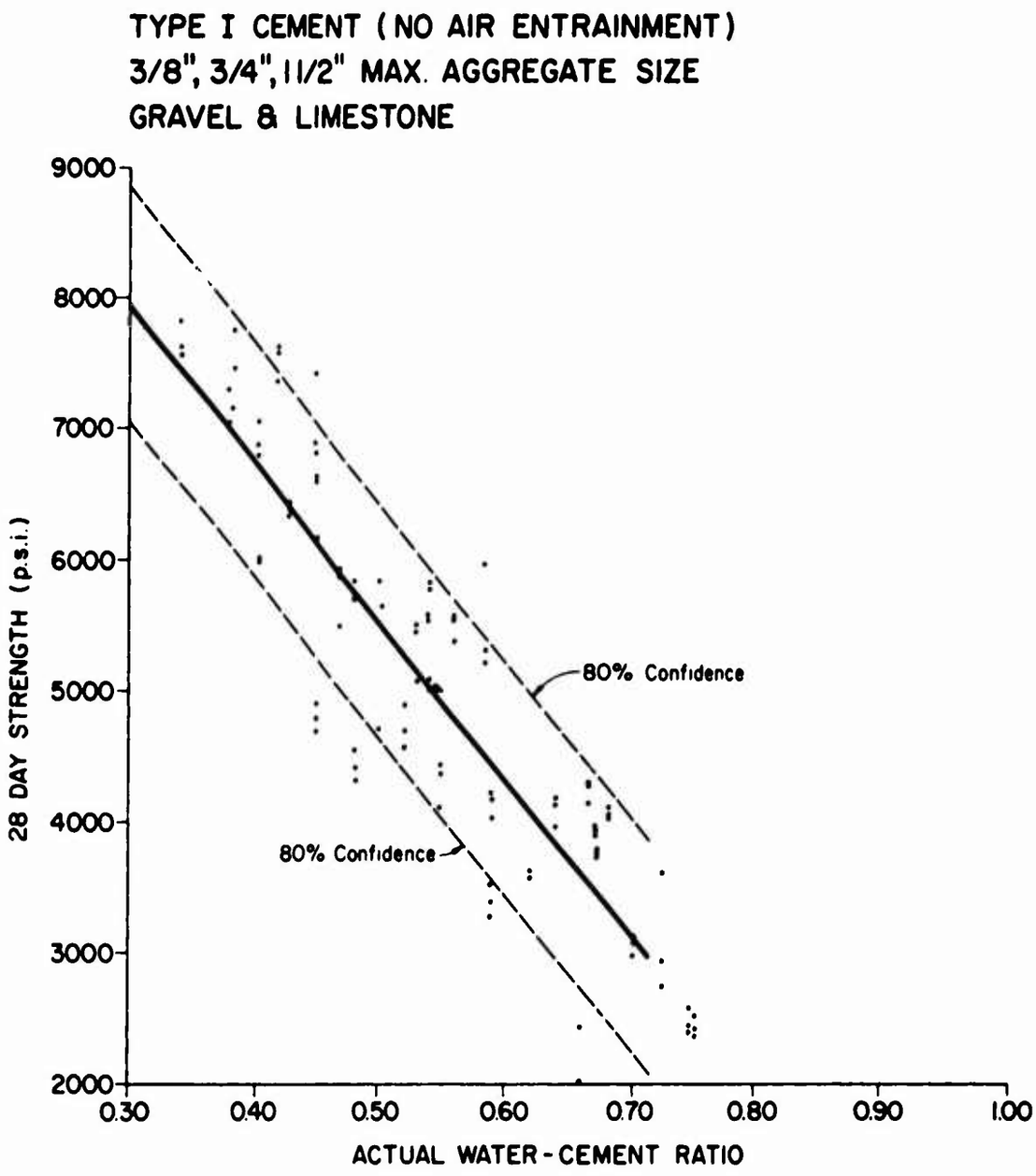

Figure 3. Actual water/cement ratio vs. 28 day compressive strength.

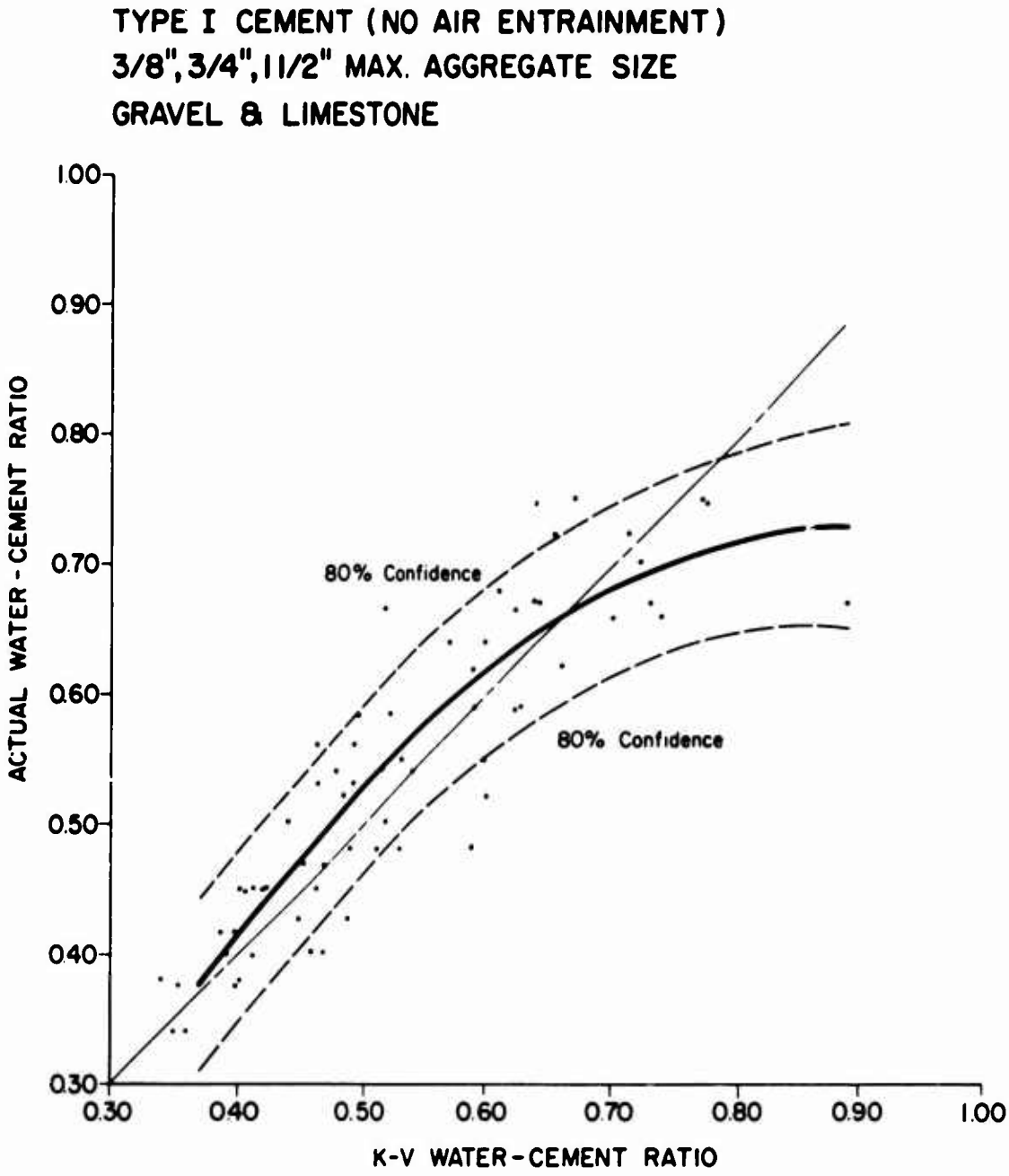

Figure 4. Actual vs. K-V water/cement ratio.

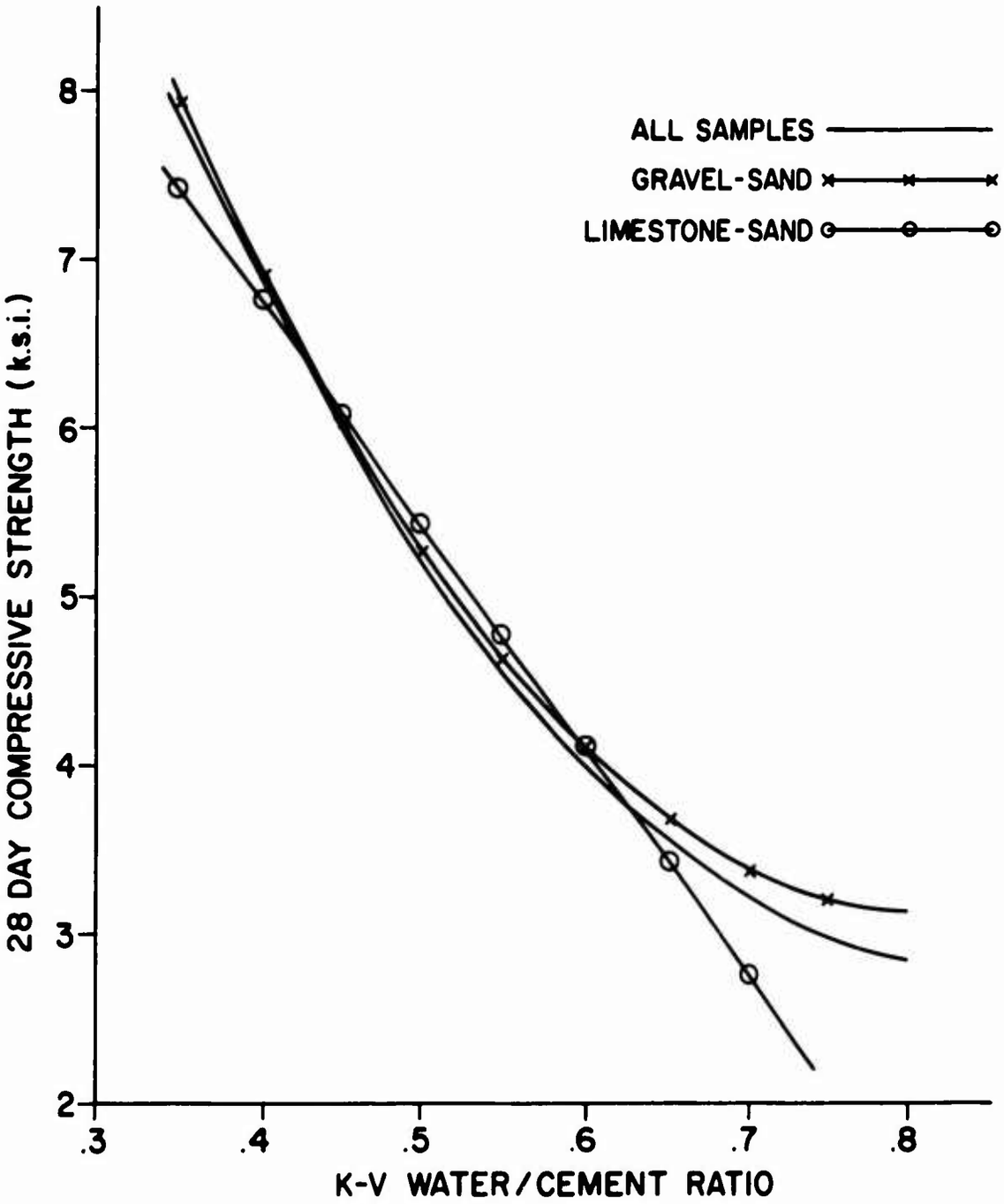

Figure 5. Water/cement ratio vs. 28 day strength (aggregate type and surface texture influence).

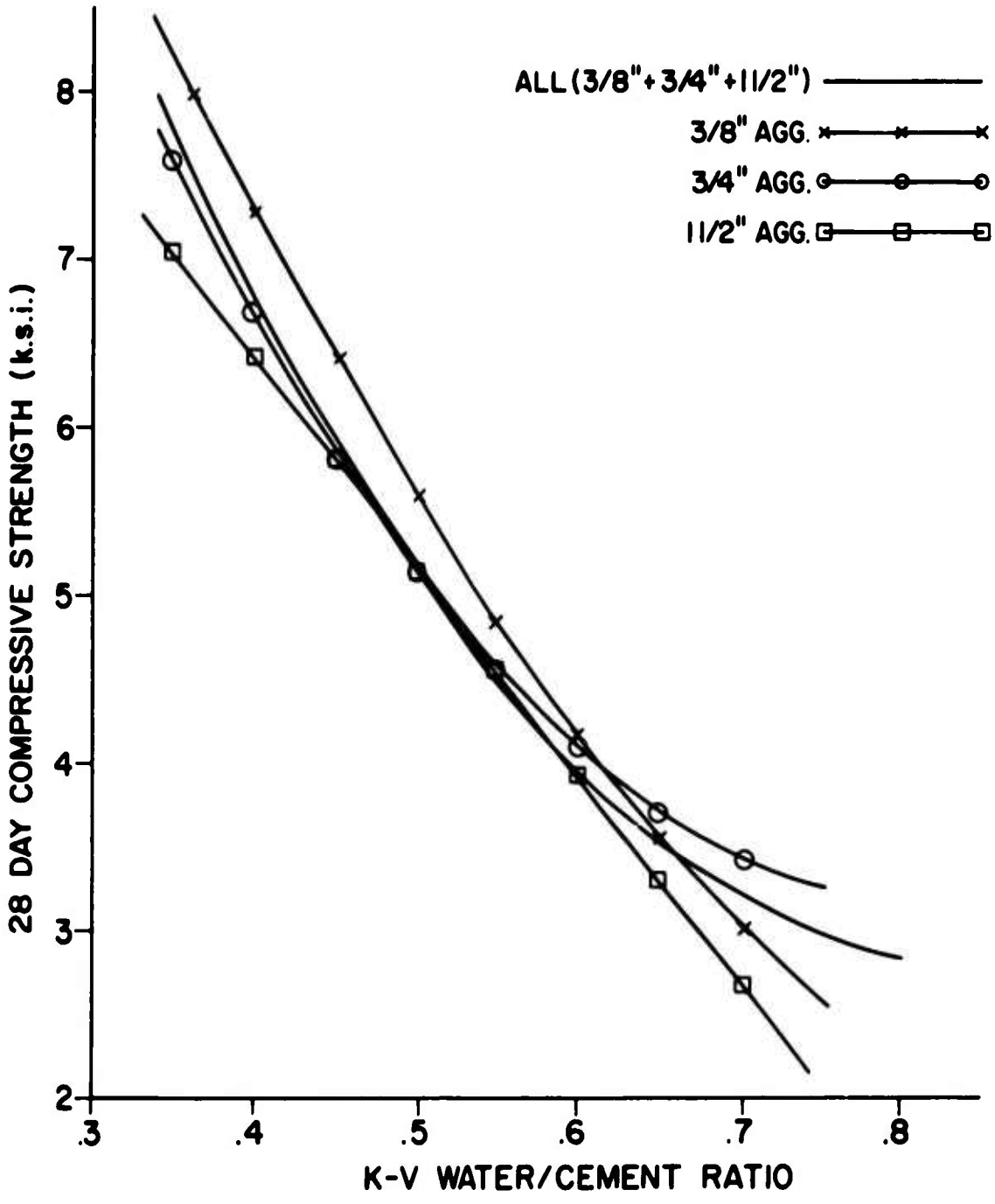

Figure 6. Water/cement ratio vs. 28 day strength (aggregate size influence).

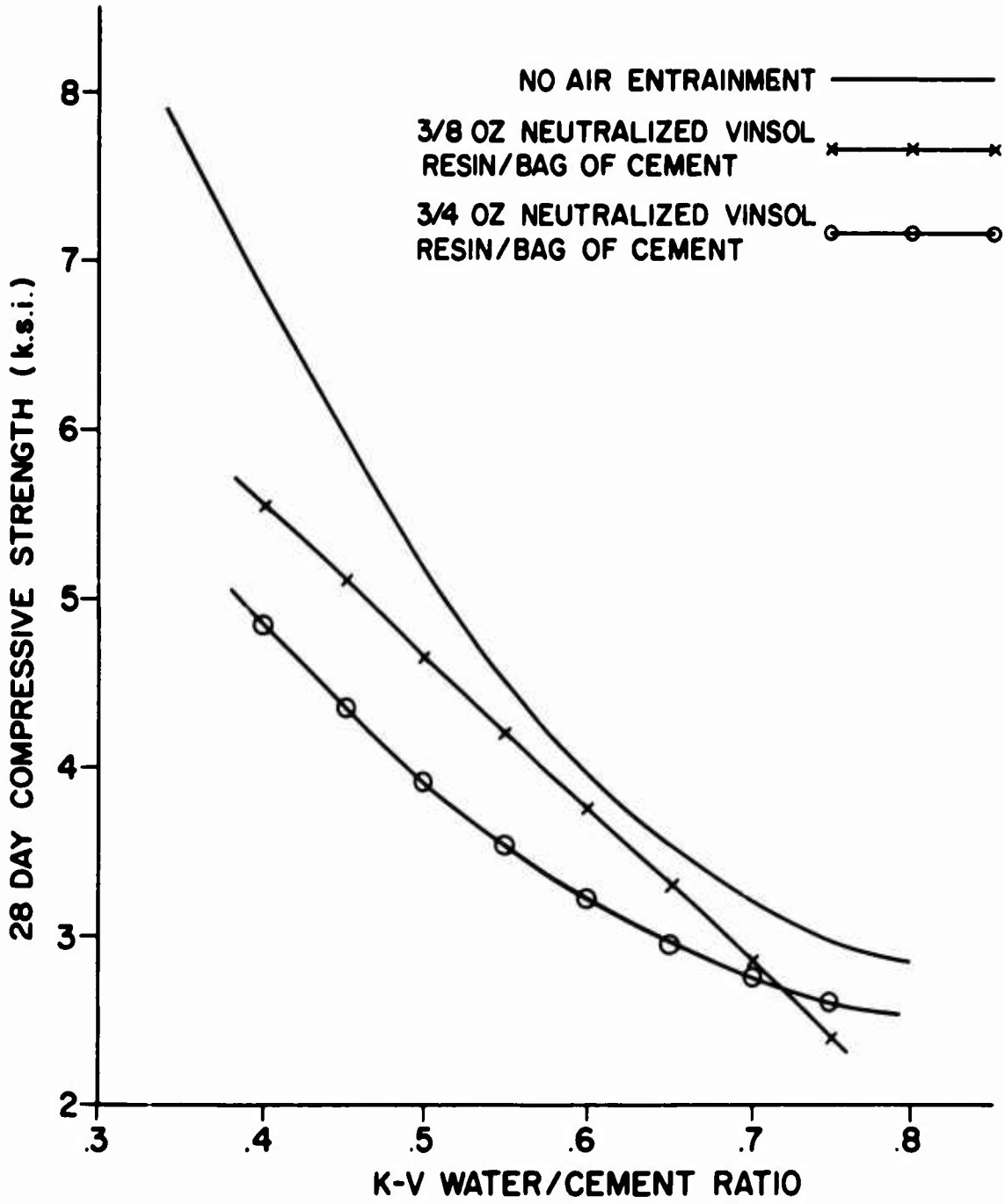

Figure 7. Water/cement ratio vs. 28 day strength (influence of air entraining agent).

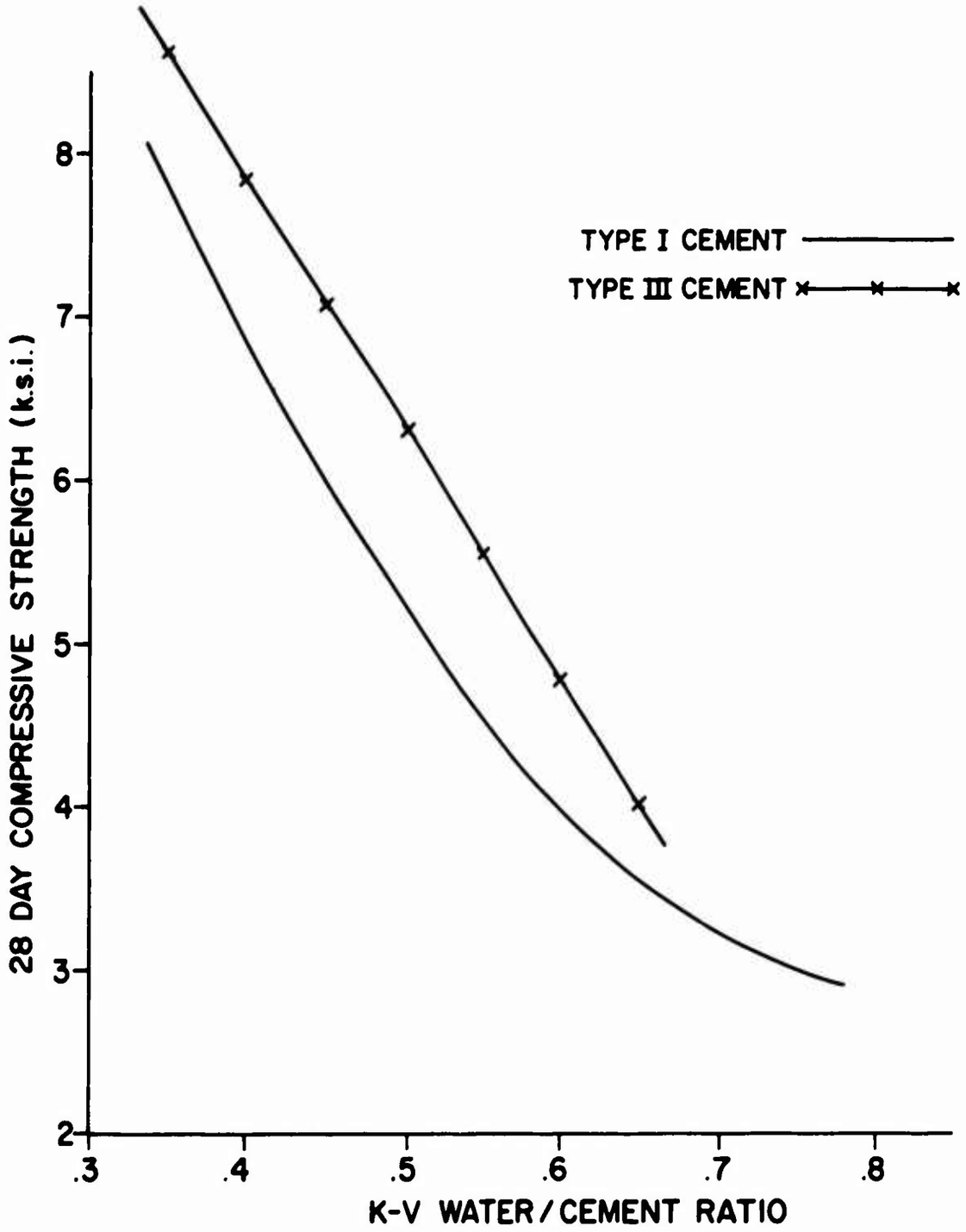

Figure 8. Water/cement ratio vs. 28 day strength (cement type influence).

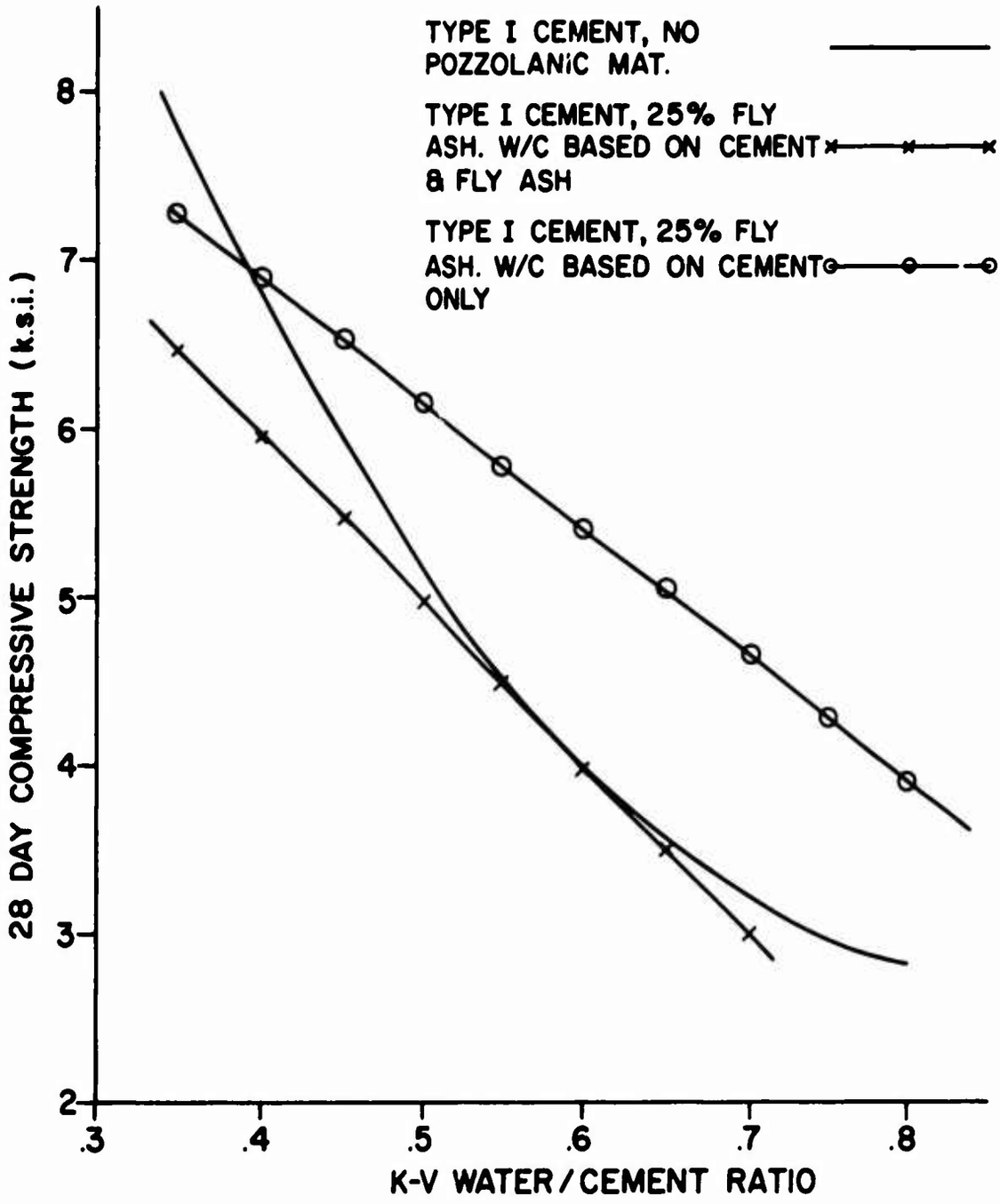

Figure 9. Water/cement ratio vs. 28 day strength (influence of pozzolanic materials).

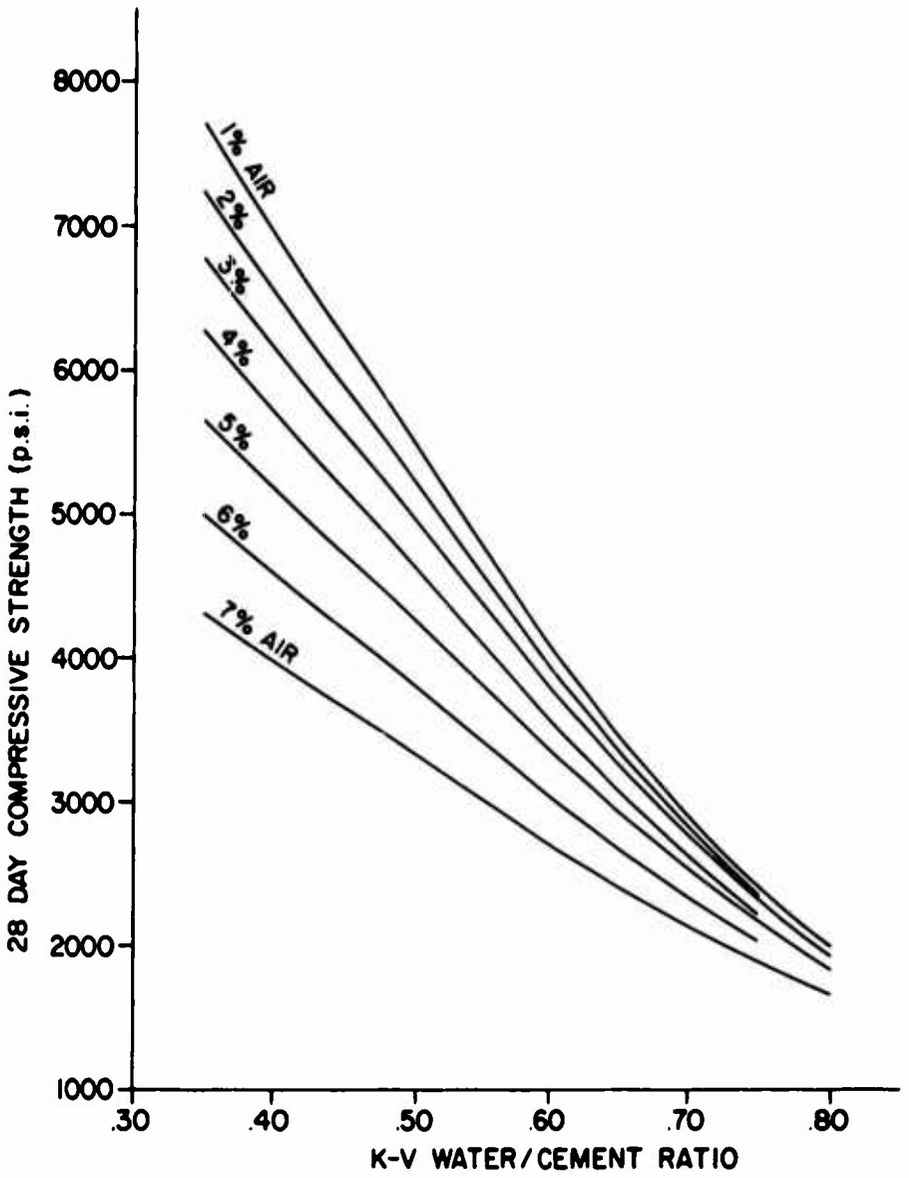

Figure 10. Strength vs. w/c and air.

HISTORY OF NUCLEAR METHODS

by

J. R. Rhodes

Manager, Applied Research Division
Columbia Scientific Industries
Austin, Texas

Presented at CERL Conference on
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ABSTRACT

This paper briefly describes the various nuclear techniques that have been considered for determining water and cement content of fresh concrete. X-ray, gamma ray, and neutron activation techniques are discussed with their relative merits described.

HISTORY OF NUCLEAR METHODS

by

J. R. Rhodes

INTRODUCTION

The development of nuclear methods for rapid, nondestructive, instrumental field analysis of fresh concrete goes back 10 years. Its chronology is interrelated with the sequence of elucidation of the techniques themselves. It also involved establishing communication between concrete technologists and nuclear physicists--groups that otherwise would hardly know of each other's existerce. This paper delineates various phases of these developments and describes the basic principles and main features of the X-ray and neutron methods.

To achieve the objective of field evaluation of the strength potential of fresh concrete, two problems must be solved. The first is to show a good correlation between the strength potential and the quantities that could possibly be measured by nuclear techniques, i.e., cement, water and aggregate contents, and bulk density. The second is to obtain sufficient accuracy and freedom from interferences for these measurements, bearing in mind that the methods under test measure element content irrespective of chemical combination--and the ingredients of concrete contain several common elements. The first problem is the business of the concrete technologist, while the second is the province of the nuclear physicist. In addition, the two groups should jointly aim to arrive at a satisfactory final result by using the simplest possible instrumentation and procedures.

The "nuclear" methods that have been considered over the years are X-ray emission, X- or gamma-ray backscatter, fast and thermal neutron activation, and prompt gamma-ray emission from thermal neutron capture (n,γ) or fast neutron inelastic scattering $(n,n'\gamma)$. It is mainly through the use of compact nuclear (radioisotope) X, gamma or neutron sources, that these techniques can be applied to rapid, instrumental analysis in the field. Thus, the availability of certain radioisotope sources, especially Cf-252, has affected the application of these techniques as much as the development of instrumentation.

CHRONOLOGY

In 1965, following development work at the Atomic Energy Research Establishment at Harwell, United Kingdom, a new field instrument became commercially available--the Portable Radioisotope X-Ray Fluorescence Analyzer. A British civil engineering group inquired into the possibility of determining cement content of fresh concrete using it. It was thought that determination of calcium by X-ray emission would yield a satisfactory measure of cement content as long as limestone aggregate was not present in significant quantities. The X-ray fluorescence method was soon ruled out, mainly because of the very low penetration of CaK X-rays (energy, 3.7 keV, mean penetration depth 0.002 cm).

The Portable XRF Analyzer is equally capable of measuring X- or gamma-rays backscattered from the sample. The backscattered photon intensity at low energies varies inversely as the effective atomic number of the sample. Since calcium is the highest atomic number major constituent in concrete the backscattered intensity can be correlated with cement content as long as other major constituents, such as water, sand and/or limestone, do not vary significantly. The higher the radiation energy, above about 50 keV, the lower the sensitivity but the greater the penetration depth. A compromise is obtained using Am-241, a long-lived source (458 yr half-life) of 60 keV gamma-rays whose mean penetration depth in concrete is 1.6 cm.

Initial experiments in Britain were not followed up. However, in 1967 the author, then at Texas Nuclear Corporation, found a United States sponsor, the Bureau of Public Roads, who with the U. S. Atomic Energy Commission funded a feasibility study of the gamma-ray backscatter method. The original intention was to use a surface probe with Am-241 together with a second measurement using Cs-137 (660 keV gamma-rays) for bulk density correction. This evolved, was simplified, and finally resulted in the single source (Am-241) depth probe described by Mitchell elsewhere in these proceedings. The feasibility study, prototype development, field trials, and manufacture and testing of the present preproduction instruments occupied the period 1968 to 1974.

Approximately concurrently with this, Frank Iddings was independently investigating the neutron activation method to measure calcium content, first with a neutron generator then with Cf-252 as it became available in 1970. Thermal neutrons activate Ca-48 to Ca-49, which decays with a half-life of 8.8 minutes, emitting 3.09 MeV gamma-rays. The big advantage of all neutron-gamma methods is that the incident neutrons and emitted gamma-rays each have a mean penetration depth in concrete of 10 cm, allowing analysis of several kg of material per reading. Problems due to particle size, heterogeneity and representative sampling are thus eliminated. However, the inherent nonuniqueness caused by the presence of calcium in both cement and calcareous aggregate was still a major problem.

In 1971 Columbia Scientific Industries proposed a multi-element analysis approach using neutron-gamma methods. The objective was to solve the limestone aggregate problem and yield a complete analysis of concrete, including water content. A feasibility study was sponsored in 1972 by the Construction Engineering Research Laboratory (CERL). This was successful and resulted in the development of a prototype instrument which was delivered to CERL in 1974 (described by Howdyshell in these proceedings).

In order to determine by elemental analysis methods, the cement and water content of concrete having an unknown siliceous to calcareous aggregate ratio a careful selection of signature elements must be made. The preferred signature elements are H (for water), Ca (for cement), C (for carbonate rock) and Si (for siliceous rock). No single neutron-gamma method can determine all these elements. In fact at least three of the four practicable neutron-gamma methods must be used. The only way to determine carbon is by fast neutron inelastic scattering $(n,n'\gamma)$ while the best way to determine H is by gamma-ray emission following thermal neutron capture. The characteristic gamma-rays in both cases are "prompt" gamma-rays and so must be measured in the presence of the neutron beam from the source. This presents special detector shielding and collimation problems. Calcium and silicon are best determined by activation analysis, the abovementioned thermal neutron reaction being used for calcium and the fast neutron reaction Si-28(n,p)Al-28 for silicon. These measurements are easier because the sample can be removed from the neutron beam for measurement of the emitted activation gamma rays.

A GAMMA BACKSCATTER AND ABSORPTION GAGE FOR THE CEMENT CONTENT OF FRESH CONCRETE

by

Terry M. Mitchell

Research Engineer, Materials Division
Federal Highway Administration

Presented at CERL Conference on
RAPID TESTING OF FRESH CONCRETE
Champaign, Illinois
May 1975

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ABSTRACT

A nuclear (gamma-ray backscatter and absorption) gage for measuring the cement content of fresh portland cement concrete has been evaluated and modified to achieve the desired accuracy and field applicability. Accuracy obtainable varies from standard errors of 22 lbs cement/yd^3 concrete (13 kg/m^3) with siliceous aggregate mixes to 31 lbs/yd^3 (18 kg/m^3) with calcareous aggregate mixes. Results reported include the effects of aggregate composition, ambient temperature, bulk density, and other parameters on gage performance. The gage is expected to be a valuable tool in the exercise of early age quality control of PCC. The author summarizes the results of the report, *A Radioisotope Backscatter Gauge for Measuring the Cement Content of Plastic Concrete*, FHWA-RD-73-48.

Two additional gages have been constructed from the Federal Highway Administration's plans and specifications and have been field-tested by state transportation departments.

A GAMMA BACKSCATTER AND ABSORPTION GAGE FOR THE CEMENT CONTENT OF FRESH CONCRETE

by

Terry M. Mitchell

INTRODUCTION

The Problem

Quality control of portland cement concrete (PCC) now depends primarily on tests such as strength measurements on cured cylinders. The results are not available until days or weeks after placement. Pre-placement control can be exercised only by overseeing the weighing-in of the cement, aggregates, admixtures, and water. In automatic batching plants which lack interlocks, however, it is almost impossible to exercise even that kind of regulation. Gravimetric control obviously leaves the final material still subject to scale errors, erratic or erroneous mixing techniques, and changes in the air and water contents of the concrete prior to placement. A rapid, simple, and accurate on-site test for the cement content--the cement factor--of wet concrete would be a valuable tool for the exercise of early age quality control of PCC.

Several test methods are available for cement factor determinations. Most, however, have been based on a physical separation (sieving) of the coarse aggregate from the mortar, followed by chemical or physical determinations of the amount of cement present in the latter phase.[1,2,3] Unfortunately such tests are usually very slow, highly susceptible to testing errors, or both.

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[1] W. M. Dunagan, "A Study of the Analysis of Fresh Concrete," *Proceedings, ASTM*, Vol 31, Part 1, (1931) pp 362-385.

[2] "Standard Method of Test for Cement Content of Hardened Portland Cement Concrete," (C 85-66), *1974 Annual Book of ASTM Standards*, Part 14, pp 42-45.

[3] R. A. Kearny and B.M.L.G. Tulloch, "Analyzing Fresh Concrete," *Concrete* (London), Vol 6, No. 3, (March 1972) pp 23-27.

The Solution

This article is a brief summary of the results of a Federal Highway Administration staff research study in which a practical "nuclear" (gamma backscatter and absorption) gage for cement content determinations was developed.[4] The overall goal of the study was to develop a gage capable of reliably and quickly determining the cement content of typical concrete mixes in the field within 28 lbs cement/yd^3 concrete (17 kg/m^3) of the actual value while the concrete is still plastic. This accuracy is equivalent to ± 0.3 sack cement/yd^3 and corresponds to about ± 5 percent of typical cement factor values for concrete used in the highway industry.

Before this study began, the Texas Nuclear Division, Nuclear-Chicago Corporation, did the basic research exploring the practicality of such a gage and constructed the first prototype. That research[5] was performed under a contract from FHWA and the United States Atomic Energy Commission. The FHWA study reported on here was organized: (1) to evaluate the acceptability of the prototype nuclear cement content gage for use in the field and (2) to make and evaluate such modifications to the gage as were necessary to meet the overall design goals.

Since August 1974, the Georgia and Maryland Departments of Transportation have been evaluating two additional prototype gages in the field. These gages were built to the detailed plans and specifications developed by FHWA. Both states are currently preparing final reports on their experience. A summary will be published later this year.

BASIC PRINCIPLES

The principles underlying the operation of the cement content gage are quite similar to those employed in the widely used nuclear density gages. Both types of gages employ gamma ray sources and detectors, but they rely on different proportions of the common gamma ray attenuation reactions.

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[4] T. M. Mitchell, *A Radioisotope Backscatter Gauge for Measuring the Cement Content of Plastic Concrete*, (Report No. FHWA-RD-73-48, Federal Highway Administration, April 1973). Available by stock number PB 224605 from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

[5] P. F. Berry, "Radioisotope X- and Gamma-Ray Methods for Field Analysis of Wet Concrete Quality," Phase II, Instrument Design and Operation, ORO-3842-2 (USAEC 1970).

In the density gage, the source, typically Cesium-137, emits high energy gammas (667 Kev). At this energy, the dominant attenuation process is Compton scattering. The amount of scattering (change of direction of the original gammas accompanied by partial loss of energy) depends primarily on the density of the scattering material. As shown in Figure 1, detection of the quantity of radiation scattered by a sample to a specific location is the basic mechanism of operation of nuclear backscatter density gages. Direct transmission density gage operation, in contrast, is based on the detection of the proportion of the original radiation remaining in an unscattered beam after it passes through a sample, as shown in Figure 2.

The cement content gage, on the other hand, employs a low energy source, Americium-241 (60 Kev), for which the photoelectric absorption process is the dominant attenuating mechanism. Compton scattering still occurs and is, in fact, necessary to divert the original radiation into the detector, as shown in Figure 3. But photoelectric absorption is a far more important determinant of how much radiation reaches the detector than is the density-dependent scattering process. The amount of absorption depends primarily on the chemical composition of the sample material and particularly on the concentrations of the elements of highest atomic number (Z). The absorption per unit path length by any single element is proportional to Z^4. Therefore, in a mixture of elements such as concrete, the per atom contribution of high-Z elements to the total absorption of gamma rays in the sample is much greater than the contribution of low-Z elements.

In concrete the attenuating medium is a mixture of cement, aggregates, and water. Calcium (Z=20), which occurs in fairly constant amounts in portland cements of various types and sources, is generally among the highest-Z elements present in significant quantities in concrete. It therefore plays a very important role in the absorption of the gammas and sensitively indicates changes in cement content.

In short, the operation of the cement content gage can be stated as follows (Figure 3): low energy gamma radiation is both scattered and absorbed by a concrete sample. The more cement present in the sample, the larger is the fraction of the original radiation absorbed and the smaller is the fraction which eventually reaches the detector to be counted.

INSTRUMENT DESIGN AND OPERATION

Design

Figure 4 shows the components which make up the most recent model of the gage. These include a polymer-impregnated concrete (PIC) test standard, a probe, a sample holder, and an analyzer. A count-ratio procedure, which employs the ratio of the count on a sample to the

count on the PIC standard as the gage-determined variable, is used to compensate for error-producing changes in the electronics with time and temperature. The probe and sample holder are also shown schematically in Figure 5. The probe contains a 14 millicurie Americium-241 radioisotope source, a 1-in. diameter by 1-in. long (25-mm by 25-mm) NaI(Tl) scintillation crystal (the radiation detector), and a high gain photomultiplier tube. The sample holder is a 1-ft^3 (0.03-m^3) unit weight bucket modified to position an annular acrylic (Lucite) spacer. The spacer reproducibly fixes the probe position relative to the concrete sample. The analyzer is a portable single channel analyzer whose main function is counting the pulses which arrive from the probe.

In addition to fixing the probe position, the spacer serves two other functions. Low energy gamma radiation has a relatively short range in concrete; those gammas which reach the detector are quite unlikely to have penetrated further than 1 in. (25 mm) into the sample. The spacer, which is relatively transparent to 60 Kev gammas, effectively increases the size of the sample sensed by the radiation before detection, thus reducing the effects of the heterogeneity of concrete samples. Of equal importance, the spacer minimizes the dependence of the gage count rate on sample density.

Operation

A single cement content determination can be completed in less than 15 minutes including the time required to fill and to empty and clean the sample holder. The skills demanded of the operator are no greater than those required by construction inspectors who use nuclear density and moisture gages. Briefly outlined, the procedure is as follows:

- After the operability of the gage is checked, the PIC standard is installed around the acrylic spacer in the sample holder. A series of 20-second counts is taken with the probe inserted in the spacer; their average is calculated and used as the "standard" count.
- The PIC standard is then removed and the sample holder is loaded with the fresh concrete sample following the standard procedure for filling unit weight buckets.
- A sequence of 20-second readings is then made with the probe at each of six vertical positions 1 in. (25 mm) apart relative to the sample. These positions are maintained by engaging the slot locating pin (see Figure 5) on the locating sleeve with each of six horizontal slots in the nylon probe support rod. The average of these six readings is then calculated for use as the "sample" count. Averaging six separate readings acts to further reduce the effect

of sample heterogeneity which would arise from the combination of large aggregate pieces and the short range of the low energy gamma radiation.

- The operator then calculates the ratio of the "sample" count to "standard" count and finds the corresponding cement content from a previously established calibration curve.

Calibration curves, such as the one shown in Figure 6, are constructed in the laboratory for each concrete job. A different curve will be obtained for concretes from each distinct aggregate source and from each ratio of coarse to fine aggregate when the two sizes are unlike chemically. Calibration curves are constructed with small, carefully controlled laboratory batches for which the actual cement factor can be established from the weights of the components. Typically mixes of three different cement factors are made. For example, for a job design cement factor of 564 lbs/yd^3 (335 kg/m^3), the calibration curve can be established with laboratory mixes of 470, 564, and 658 lbs/yd^3 (279, 335, and 390 kg/m^3, respectively).

Detailed information on the instrument design and operation can be found in the operating manual for the gage[6] which will be published later in 1975.

SUMMARY OF GAGE FEATURES

- Components - four (sample holder, probe, analyzer, and PIC standard).
- Total weight - 69 lbs (31 kg).
- Total test time - less than 15 minutes per sample.
- Total counting time - 2 minutes.
- Precision - 5 lbs cement/yd^3 concrete (3 kg/m^3).
- Accuracy (standard error; single sample) - 22 to 31 lbs/yd^3 (13 to 18 kg/m^3).
- Operation - 20 hours from rechargeable silver-cadmium batteries or continuous 110 V AC line operation.
- Full battery recharge time - 15 hours.

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[6] T. M. Mitchell, *Instruction Manual - Nuclear Cement Content Gage*, (Federal Highway Administration [in publication], 1975).

- Operating temperature range - 35 to 120°F (2 to 49°C).
- Radiation hazards - minimal.
- Digital readout on analyzer - converts to cement factor with use of laboratory constructed calibration curve.
- Gage response - independent of concrete bulk density, water content, and air content.

RESULTS

The results reported here are those obtained during FHWA's laboratory evaluation of the cement content gage. The laboratory evaluations have considered all of the parameters which are expected to significantly affect gage performance, including aggregate composition, gage temperature, bulk density, and water content.

Aggregate Composition

The earliest results with the Texas Nuclear prototype gage indicated that aggregate composition would pose some difficulties in the operation of the cement gage. As explained previously, the gage's sensitivity to cement content depends on both the level of calcium in the concrete and that of other high atomic number (Z>20) elements in the aggregate. It was anticipated that large quantities of calcium and other high-Z elements in an aggregate would result in low count rates from concretes made with the material, reduced sensitivities (changes in count rate per unit change in cement content), and less accurate cement content determinations.

Two coarse aggregates were employed in the main part of the evaluation, one siliceous (a river gravel) with very little intrinsic high-Z material, the other calcareous (a dolomitic limestone) with more than 20 percent calcium. Mixes with each over a range of cement factors (450 to 670 lbs/yd^3 - 270 to 400 kg/m^3) and densities (136 to 150 lbs/ft^3 - 2180 to 2400 kg/m^3) gave a standard error for cement factor determinations of 22 lbs/yd^3 (13 kg/m^3) for the siliceous aggregate mixes and 31 lbs/yd^3 (18 kg/m^3) for calcareous aggregate mixes. (Note: The standard error is the root mean square of the differences between the cement factor as determined with the nuclear gage and the actual cement factor of a batch as determined from the weights of the components.) When the cement factors of three samples from the same batches were averaged, the standard error of the determinations was reduced to 19 lbs/yd^3 (11 kg/m^3) for the siliceous aggregate mixes and 22 lbs/yd^3 (13 kg/m^3) for the calcareous aggregate mixes.

Additional data were recorded with two other nominally siliceous aggregates from California. These contained sizeable quantities of iron (Z=26), titanium (Z=22), and calcium (Z=20), and one contained several hundred parts per million (ppm) of barium (Z=56). Because of its high atomic number, 163 ppm of barium has a gamma absorption equivalent to 1 percent of calcium. Mixes with these aggregates confirmed the hypothesis that concretes containing calcium and significant quantities of other high-Z elements will show reduced gage sensitivity to changes in cement content and will give less accurate cement factor determinations.

Separate calibration curves must be generated for individual aggregate sources because of the indicated sensitivity of the cement content gage to chemical composition. In addition, whenever the coarse and fine aggregates in a mix are of significantly different chemical compositions, a separate calibration curve is required for each significant change of their relative proportions in a mix design.

Temperature

The other major parameter which affects the gage's performance is its temperature. Changes in the gain of the photomultiplier tube and in the analyzer electronics with temperature produce significant changes in gage count. Data indicated that, when no temperature compensation was available, the error in a cement factor determination made at 40°F (4°C) caused by using a calibration curve generated at 72°F (22°C) was approximately 170 lbs/yd^3 (100 kg/m^3).

In the model of the gage described here, temperature compensation is achieved by the use of the count-ratio method with the PIC standard. When counts on a fresh concrete sample and on the PIC standard are taken at roughly the same time and temperature, experimental results have indicated that the temperature effects will approximately cancel out when the ratio of the two counts is used as the gage-determined variable.

Other Variables

On theoretical grounds, the bulk density of concrete samples was expected to significantly affect gage performance and did, in fact, in the Texas Nuclear prototype evaluation. For the most recent gage model, data taken over a range of densities typical for highway concretes--136 to 150 lbs/ft^3 (2180 to 2400 kg/m^3)--indicated no significant dependence of count on density when cement factor was held constant.

The cement content gage response does not vary with either water content or air content over the usual range of those variables in highway concrete.

SUMMARY AND CONCLUSIONS

A nuclear gage for determining the cement content of plastic (fresh) PCC has been developed and evaluated. The results indicate that the gage establishes cement factors to the accuracy needed for structural concrete on highway projects.

FHWA's Offices of Research and Development foresee a number of practical applications for a test method based on the use of this gage. The most important obviously is insuring that PCC delivered to a construction site has the proper cement content, thereby providing improved job control. The gage could also be used in the qualification of PCC mixing equipment and procedures, and it will be a valuable aid in field or laboratory research investigations on concrete.

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"Standard Method of Test for Cement Content of Hardened Portland Cement Concrete," (C 85-66), *1974 Annual Book of ASTM Standards*, Part 14, pp 42-45.

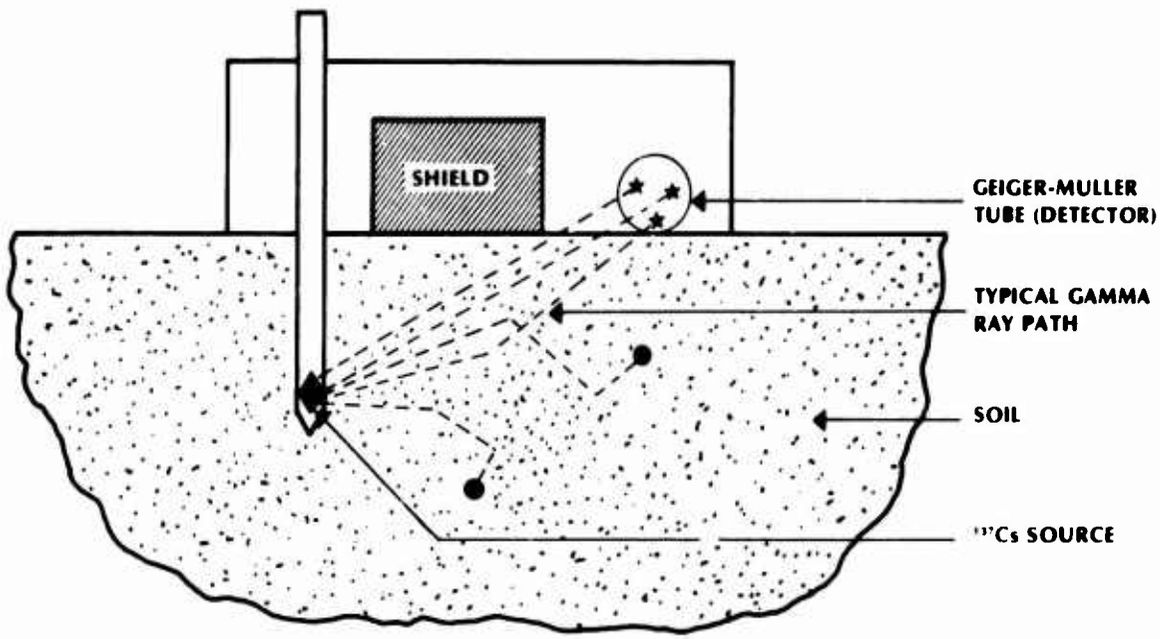

Figure 1. Nuclear density gauge, backscatter type.

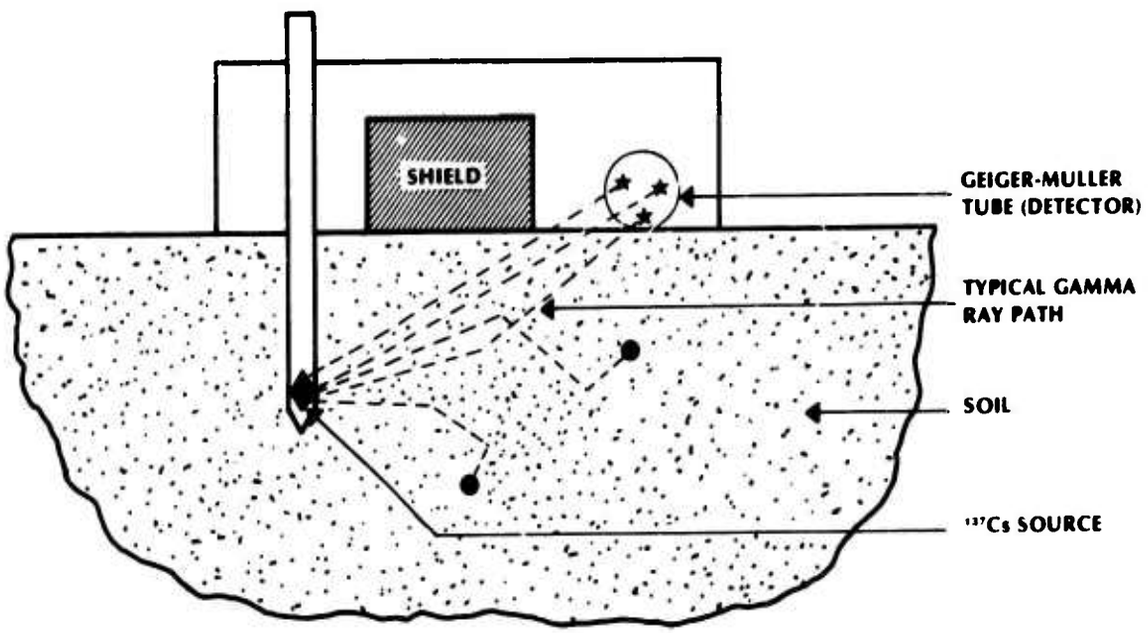

Figure 2. Nuclear density gauge, direct transmission type.

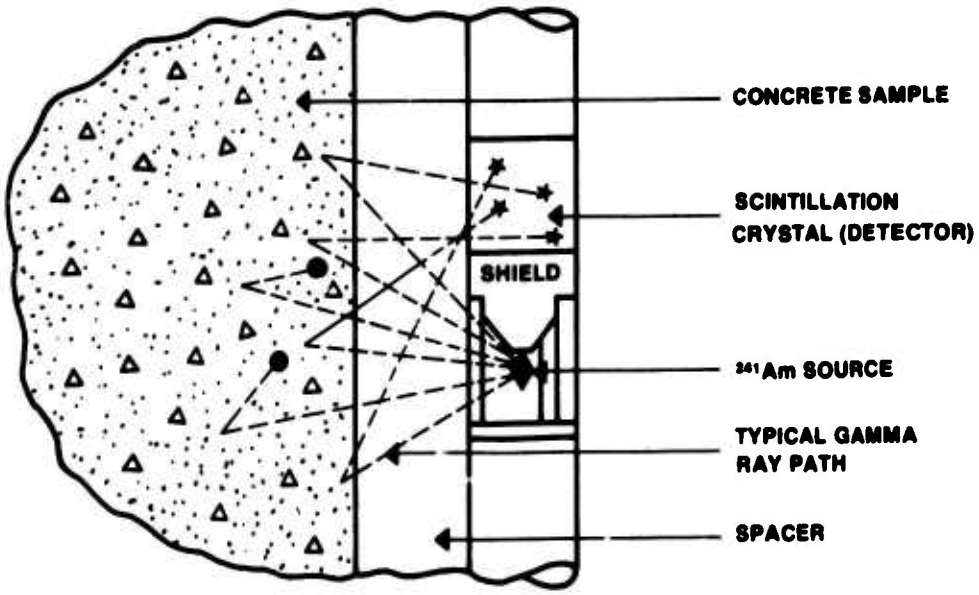

Figure 3. Nuclear cement content gauge.

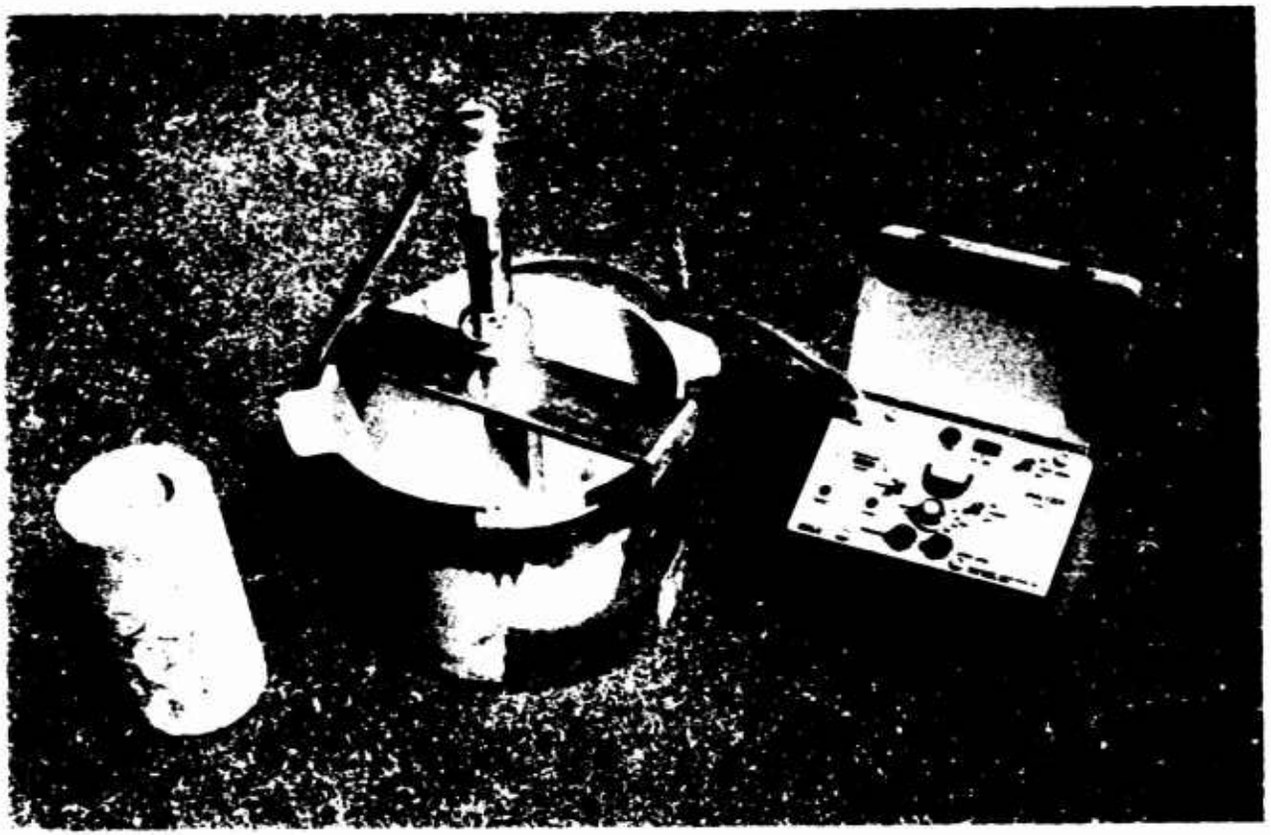

Figure 4. Cement content gauge: PIC test standard, sample holder and probe, analyzer.

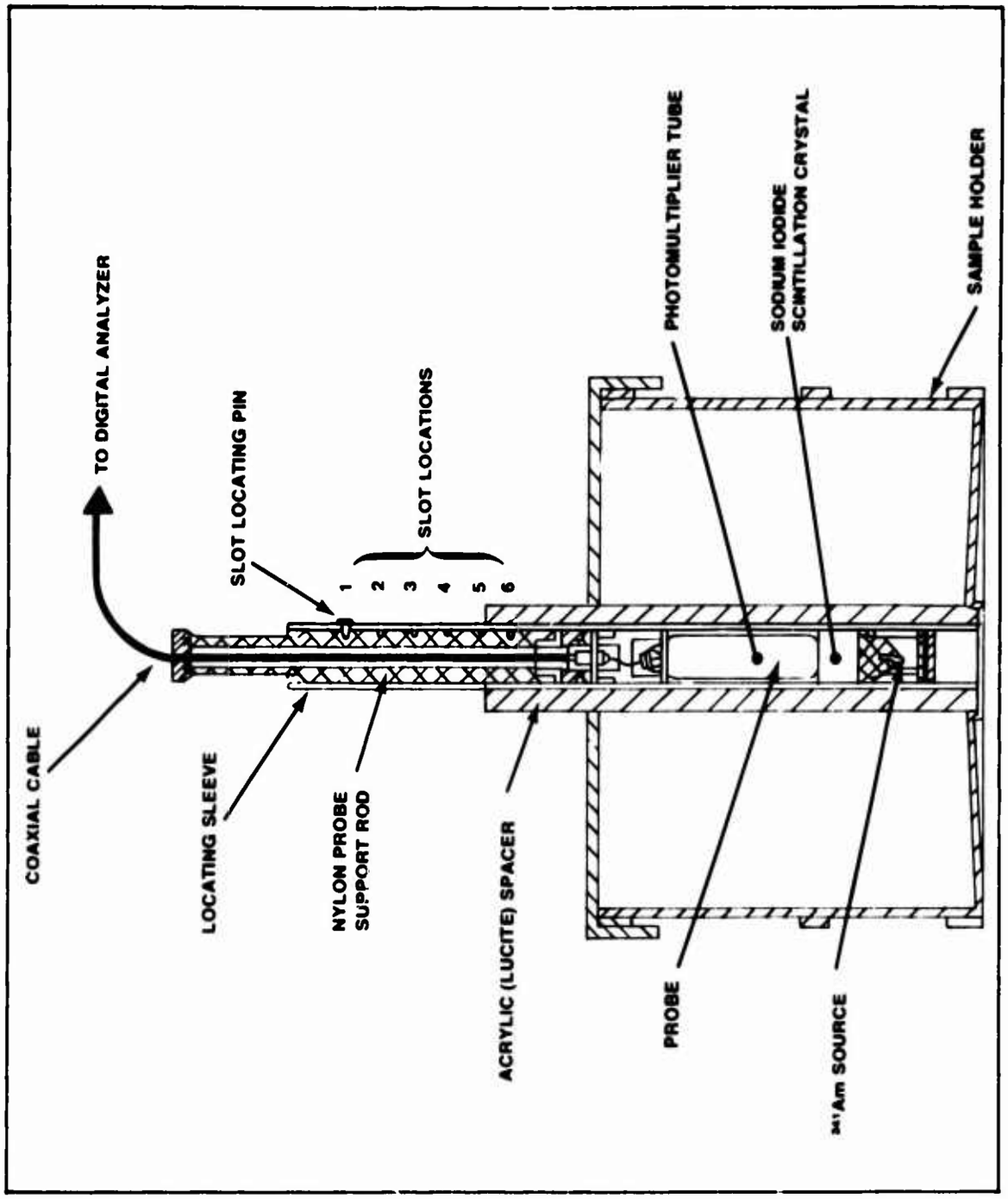

Figure 5. Schematic, sample holder and probe.

Errata Sheet for CERL Conference Proceedings M-128,
Rapid Testing of Fresh Concrete.

Graph below should replace Figure 6 on page 104.

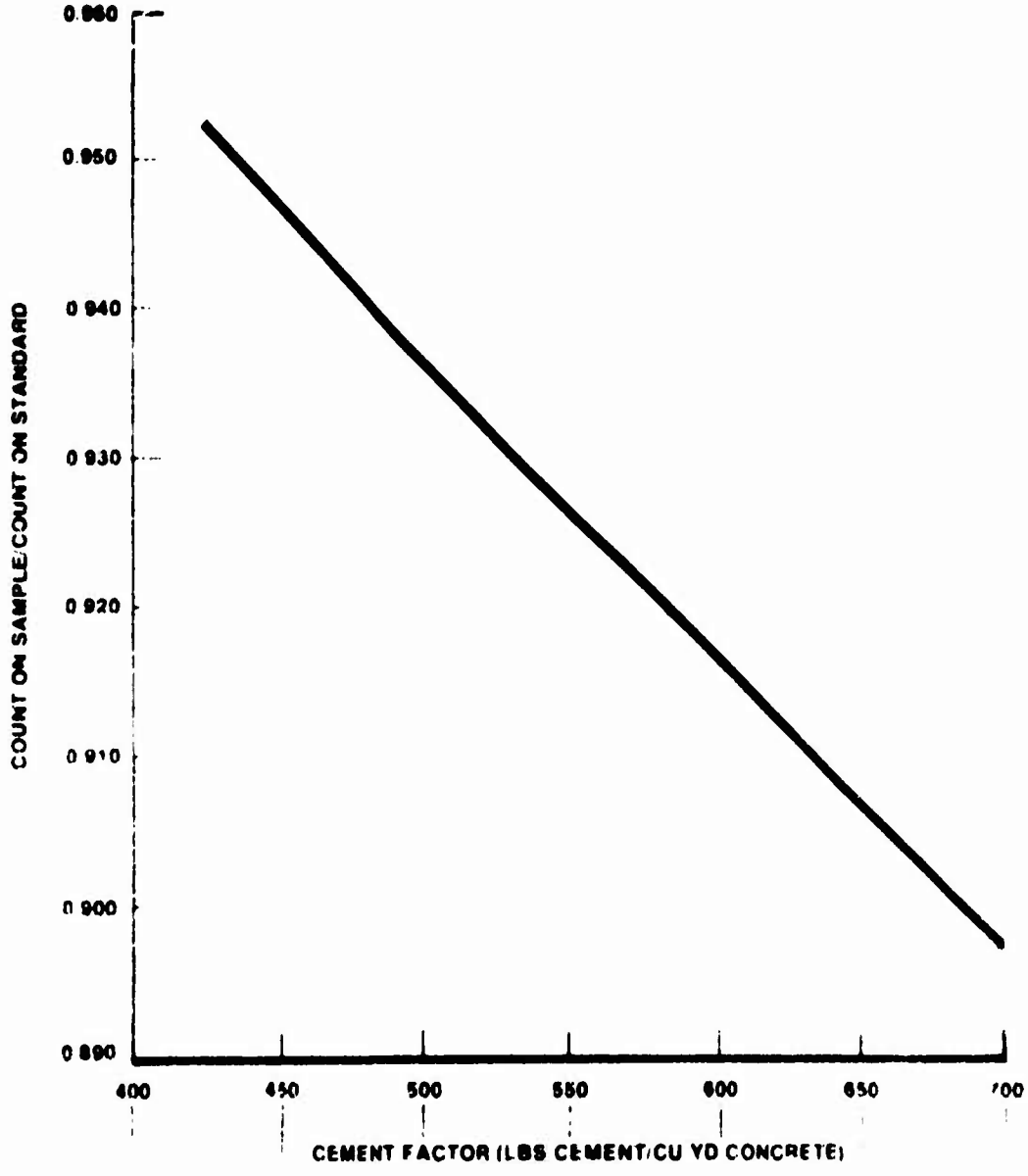

Figure 6. Typical calibration curve -- coarse aggregate Riverton, VA, limestone.

ANALYSIS OF IN-PLACE AND PLASTIC CONCRETE FOR CEMENT CONTENT BY NEUTRON ACTIVATION ANALYSIS

by

Frank A. Iddings
Ara Arman
Calvin E. Pepper
Winton G. Aubert
John R. Landry

Nuclear Science Center
Louisiana State University
Baton Rouge, LA

Presented at CERL Conference on
RAPID TESTING OF FRESH CONCRETE
Champaign, Illinois
May 1975

ABSTRACT

Results from neutron activation analysis of in-place and plastic concrete samples are presented. Data were obtained by equipment suitable for and operated under field conditions. The system described for determination of cement content of in-place concrete includes a 35 microgram Cf-252 source, portable activation/shield assembly with remote operating cable, and commercially available detector and electronics. An analysis of in-place concrete is accomplished in 22 minutes.

Plastic concrete results were obtained using a system designed for soil-cement mixtures. Using a 140 microgram Cf-252 source, and analysis could be completed in 9 minutes with an accuracy of ±5 percent of the amount of cement for normal cement contents. A system for analysis of samples of plastic concrete, cores, and soil-cement is described that can be moved to field sites in a trailer.

Most existing methods for determination of cement content of concrete suffer from being too slow, using too small a sample to be representative, and having to be done in a laboratory. The only other field measurement technique being studied uses low energy photon scatter. This technique uses only a thin layer of the available sample and fails to achieve necessary accuracy when aggregate varies in size distribution or heavy element content.

Neutron activation analysis offers a rapid, field-operational, and simple procedure for measurement of cement content. Besides the advantages above, activation analysis allows the use of large, representative samples and offers considerable freedom from interferences.

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THEORY

Exposure of a sample of concrete to neutrons produces measurable quantities of a number of radioactive isotopes. By controlling the neutron energy spectrum, time of activation (neutron bombardment), decay time, measurement time, and instrumental settings, certain of the radioactive products representing cement content can be emphasized. For a fixed set of conditions, radioactivity and composition are directly related. The strict relationship between radioactivity at the end of neutron activation and composition is

$$A = \frac{(\text{weight of element})\ (6.02 \times 10^{23}) a\ b\ c\ [1 - e^{-0.693(t/T)}]}{\text{Atomic weight of element}}$$

where

A = activity in disintegrations/sec

a = abundance of the reacting isotope of the element

b = bombarding neutron flux in neutrons cm^{-2} sec^{-1}

c = cross section or probability of reaction in cm^2

t = activation time

T = half-life of radioisotope produced.

This relationship simplifies for fixed experimental parameters such as sample size and geometry as well as those mentioned above:

Counts = K (percent cement)

Counts = disintegrations measured by instrumentation

K = a constant for the fixed conditions selected

Such a relationship permits formation of a graph, such as Figures 1 and 2, relating counts and cement content. Standard samples treated exactly like samples for the fixed experimental parameters generate the graph for a specific set of components.

EXPERIMENTAL PARAMETERS

Table 1

Ratioactive Isotopes Produced in Concrete by Short Duration Neutron Bombardment

Radionuclide	Half life	Gamma Energy(MeV)
Al-28	2.3 minutes	1.78
Ca-49	8.8 minutes	3.09, 4.05
K-42	12.4 hours	1.52
Mg-27	10.0 minutes	0.84, 1.02
Mn-56	2.58 hours	0.84, 1.81, 2.13
Na-24	14.8 hours	1.37, 2.75

Table 1 lists the radioactive materials produced in appreciable quantities by short-duration neutron bombardment. Of these observed radio-nuclides, Ca-49 represents cement content better than any other. In areas using siliceous aggregate and sand, the Ca-49 is indicative of only the cement content. By instrumental discrimination against gamma energies below 2.5 MeV, only Ca-49 and Na-24 produce counts. By using short nuetron bombardment, decay, and counting times, Ca-49 activity greatly exceeds Na-24 activity. Note in Figure 3 that Ca-49 is observed in the gamma spectrum above 2.5 MeV. With large neutron sources, the typical analysis schedule includes a 5-minute neutron bombardment or activation, 1-minute decay for transfer of the sample to counting instrumentation, and a 5-minute counting or measurement period. For small neutron sources or small samples, the schedule may lengthen to 10:2:10 minutes for activation: decay: count.

The counting mentioned above follows the procedures and

instrumentation established for soil-cement mixtures.[1,2,3,4] A 12.7 cm x 12.7 cm NaI(Tℓ) crystal detects the gamma radiation. Thermal insulation, shock mounting, and neutron shielding protect the crystal for field use. The large crystal gives the sensitivity necessary for detection of the 3.08 Mev gamma radiation from the small quantity of Ca-49 produced. Smaller crystals can be used but require substantially larger neutron sources along with longer activation and counting times.

The associated electronic instrumentation consists of a tube base with high voltage divider network fitted to the detector and connected to a single-channel-analyzer scaler system by a single coaxial cable. The scaler system provides high voltage for the detector operation and permits selection of the gamma energies to be included in the measurement. The discriminator of the single-channel-analyzer rejects gamma energies below those of the Ca-49. A convenient prepackaged scaler system is the Eberline Instrument Co. model MS-1. The MS-1 system operates adequately for laboratory and field use since it can accept either 110VAC or 12VDC (auto battery) power. Field counting systems are shown in Figures 4 and 5.

The most compact, high output, and constant yield neutron source available for activation of the concrete samples in the field is Cf-252. The Cf-252 decays by alpha emission and spontaneous fission. The fission produces a broad energy spectrum of neutrons. This broad energy spectrum of neutrons permits deep penetration into the sample. Figure 6 indicates the thickness of concrete sample producing useful information on cement content. Figure 7 indicates the increase in analytical signal with sample area at constant thickness. These data mean that the analytical information comes from several kilograms of sample material. Such a sample has a good chance of being representative of the bulk of material.

The inner construction of the activation/shield assembly for

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[1] F. A. Iddings, Ara Arman, A. W. Perez II, D. W. Kiesel, and J. W. Woods, "Nuclear Techniques for Cement Determination," *Highway Research Record* No. 268, pp 118-130 (National Academy of Sciences, 1969).

[2] F. A. Iddings, L. W. Miller, Jr., and C. E. Pepper, "A Rapid Field Determination of Cement Content," *Proceedings of the 9th Symposium on Nondestructive Evaluation*, pp 127-131 (Southwest Research Institute, 1973).

[3] F. A. Iddings and Ara Arman, *Determination of Cement Content in Soil Cement Mixtures and Concrete* Interim Report on Contract 736-01-52, (Division of Engineering Research, Louisiana State University, July 1973).

[4] P. A. Howdyshell, *Laboratory Evaluation of a Chemical Technique to Determine Water and Cement Content of Fresh Concrete,* Technical Report M-97 (Construction Engineering Research Laboratory, July 1974).

analysis of *in-place concrete* is shown in Figure 8. This assembly rolls to the site of the analysis and stands on end for activation of the surface of the concrete. The activation with neutrons begins when the Cf-252 source (about 35 micrograms) moves from storage position to a point 1.25 in. (3.2 cm) from the end of the assembly. The source moves when the operator turns a crank attached to the source by a flexible cable (such as used in isotope radiography). The crank and cable arrangement removes the operator to a safe, low radiation exposure position remote from the activation position. Figure 9 shows the activation/shield assembly in an activation position on top of a calibration slab of concrete. Calibration slabs are 20 in. x 20 in. x 5 in. (56 cm x 56 cm x 12.5 cm) in size. The remote crank-out and cable are visible behind the assembly.

The source size, 35 micrograms of Cf-252, arose from the need to have an easily portable system combined with a need for rapid analysis. The present system can be moved and operated by one man although a two-man crew is desirable. Any larger source of Cf-252 would require a shield too heavy for easy use.

The activation/shield assembly for plastic concrete must house a larger source for rapid results. A compromise between speed and source size (cost and shielding) gave the assembly drawn in Figure 10. This assembly holds a 150 microgram Cf-252 source. As noted, this assembly also uses a moving source. The source moves to an activation position below the sample on a wheel by the operator turning a crank on the side of the shield. Samples sit on the top of the unit inside a series of "donuts" to accommodate samples from 2 liter cylindrical cardboard cartons to those contained in large polyethylene buckets. These large samples are over 20 centimeters in diameter and are about as large as can be handled by one person. While this assembly can be moved on rollers, its portability will be confined to a small trailer for field work.

With proper "donut" adapters, the activation/shield assembly can also be used for activation of soil-cement samples and standard core samples. Adapters must be used to keep radiation intensity at the operator position at a safe level. The detector system for all these samples is shown in Figure 4.

RESULTS

Operation of the in-place concrete analysis system in the lab using carefully prepared standard slabs produced the results shown in Figure 1. The slabs cover the range from 4 to 7 bags of cement per cubic yard of concrete. Their physical size is 20 in. x 20 in. x 5 in. (56 cm x 56 cm x about 12.5 cm) with some variation in thickness. Designations of A, B, and C groups of samples mean separately mixed

batches of each composition. Corrections for variation in thickness (see Figure 6) are applied to the results.

Results on plastic concrete include only laboratory measurements. Figure 2 illustrates the results obtained on cylindrical samples using a 140 microgram Cf-252 source. The standard deviation (1 σ or 68 percent confidence) for each set of five different samples represents a variation of less than 5 percent *of the amount of cement* measured; i.e., 10.0 ± 0.5 percent cement.

CONCLUSIONS

For siliceous aggregate and sand samples of concrete, cement content is rapidly and accurately measured by neutron activation analysis. Both in-place and plastic samples can be analyzed in field as well as in laboratory environments. Commercially available electronic systems and sources are adequate. Activation/shield assemblies must be fabricated by user or specialty companies since they are not yet commercially available items.

ACKNOWLEDGEMENT

The authors wish to express appreciation to L. W. Miller, Jr., Orren Williams, and James Melancon for their technical assistance and to the U. S. Department of Transportation, Federal Highway Administration, and the Louisiana Department of Highways for technical and financial support.

The opinions, findings and conclusions expressed in this paper are those of the authors and not necessarily those of the Department of Highways or Federal Highway Administration.

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F. A. Iddings, Ara Arman, A. W. Perez II, D. W. Kiesel, and J. W. Woods, "Nuclear Techniques for Cement Determination," *Highway Research Record* No. 268, pp 118-130 (National Academy of Sciences, 1969).

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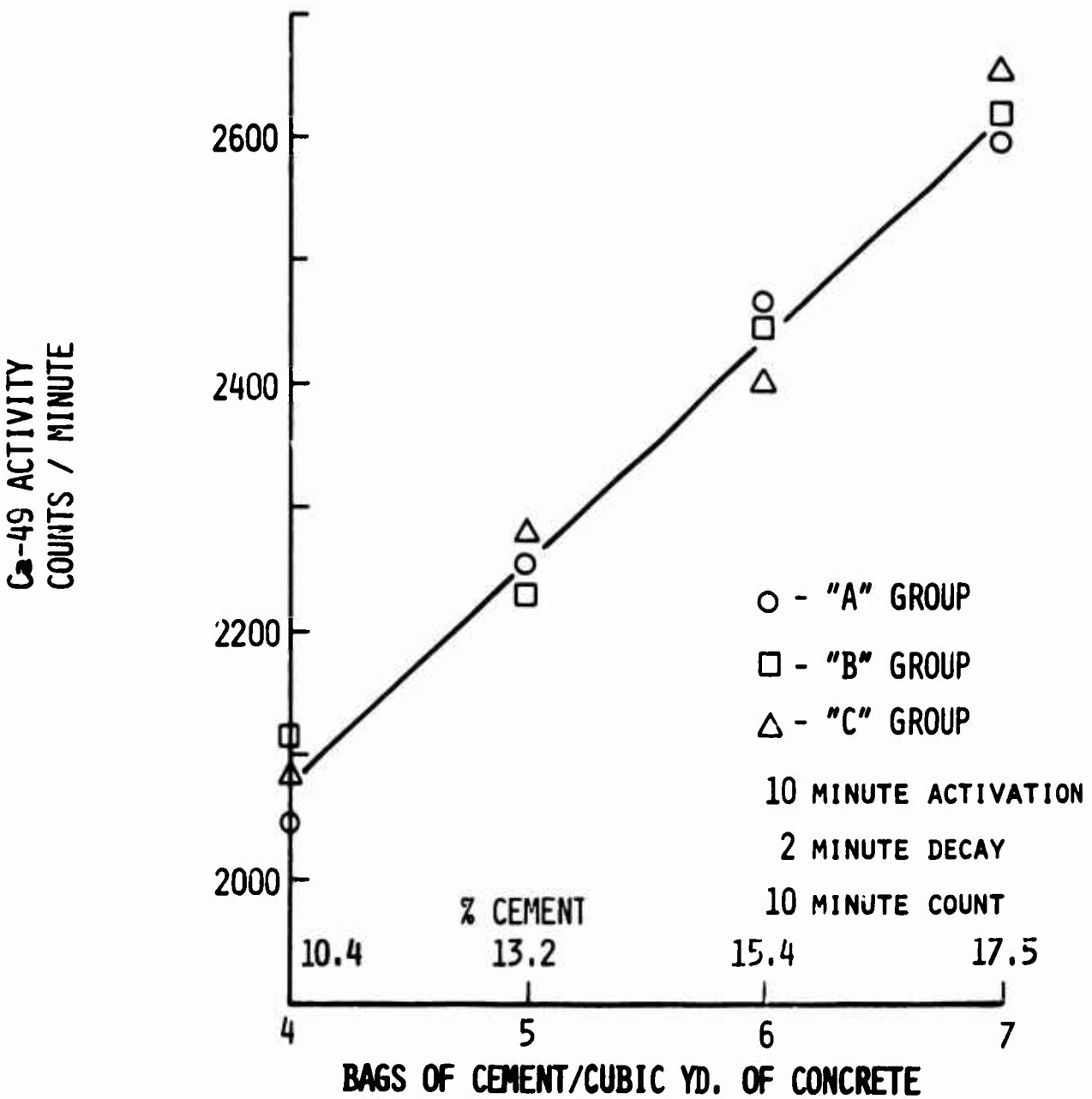


Figure 1. Laboratory analysis of "in-place" concrete slabs.

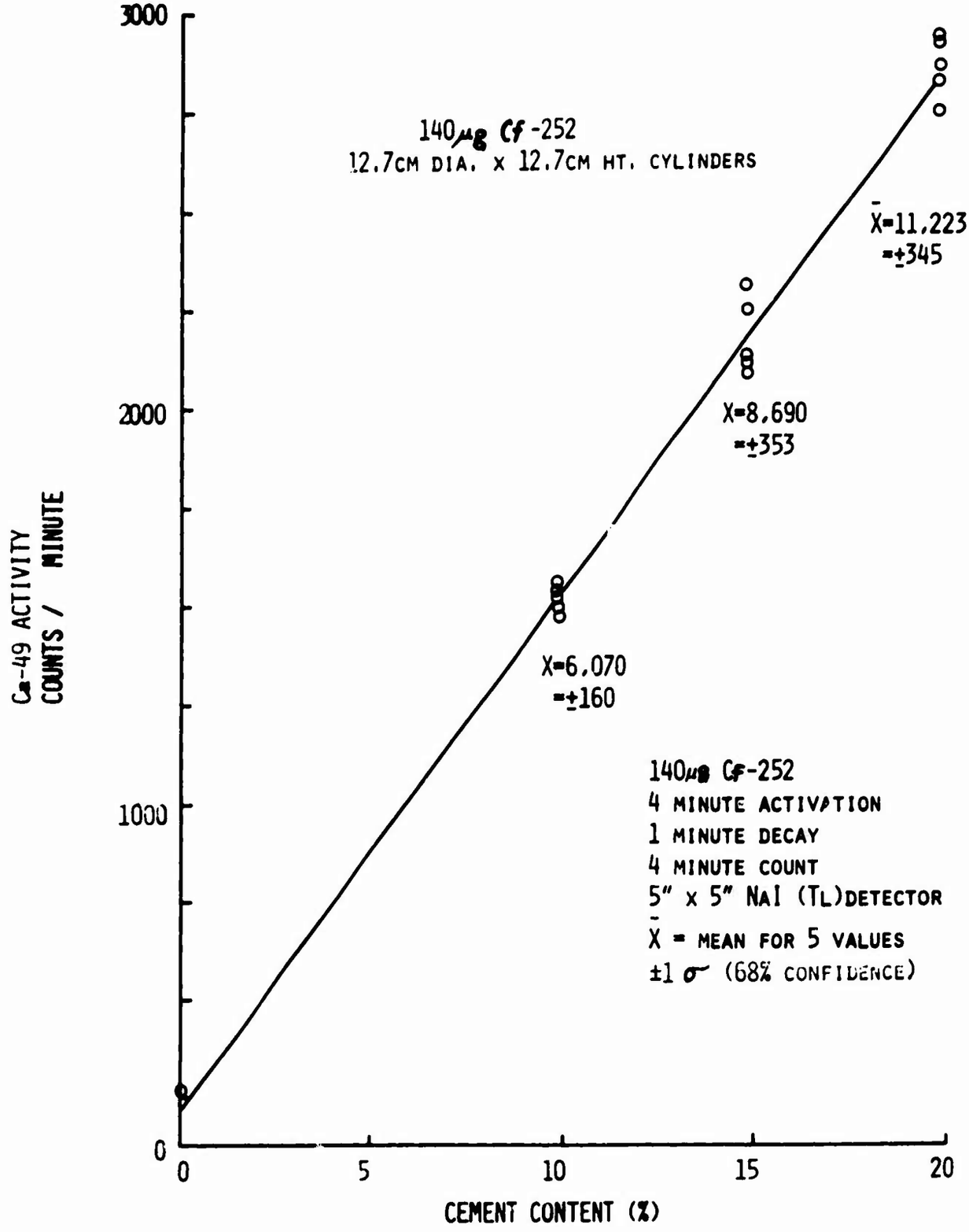


Figure 2. Determination of cement content in plastic concrete samples using soil-cement field system.

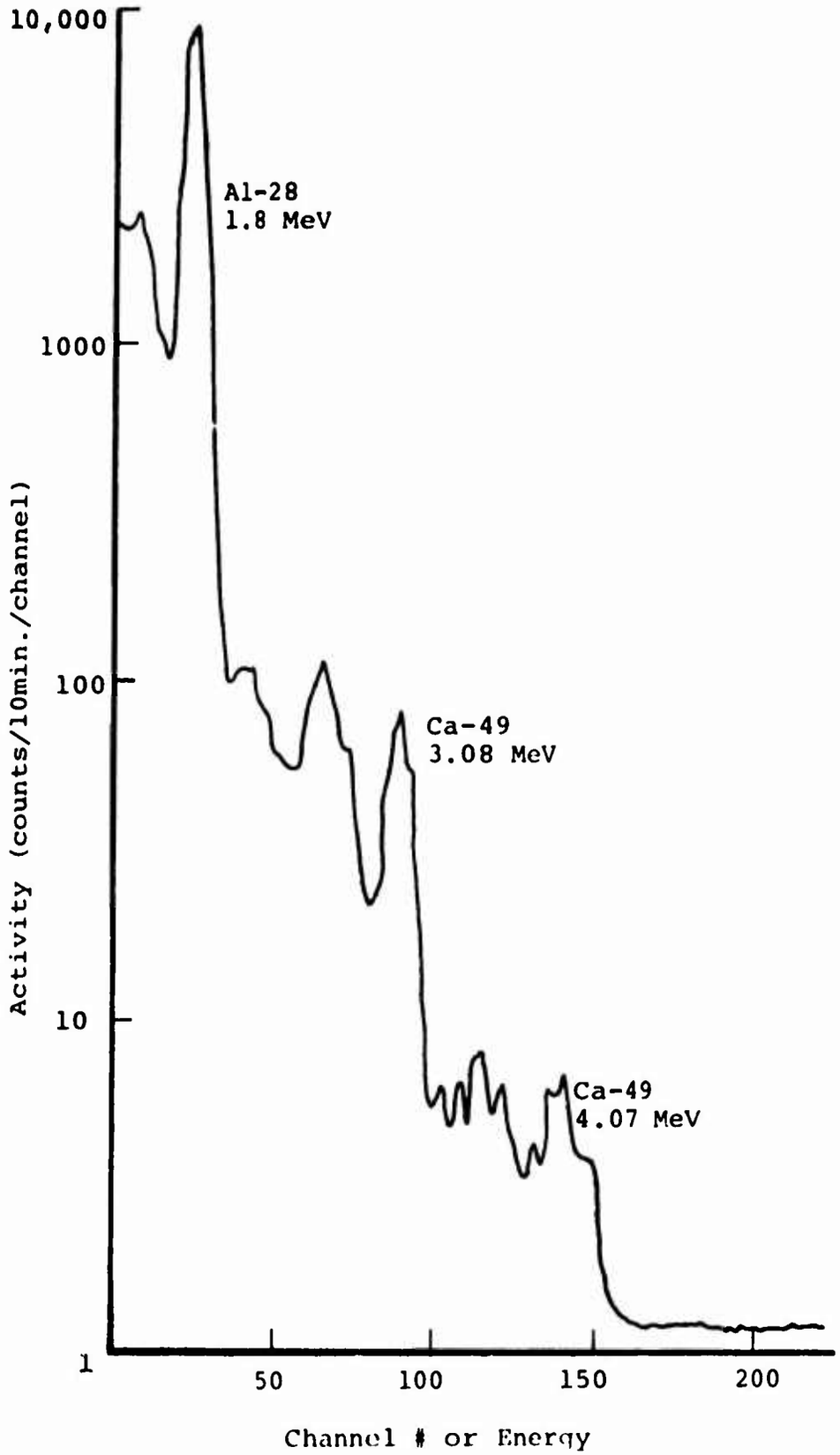


Figure 3. Concrete gamma spectrum.

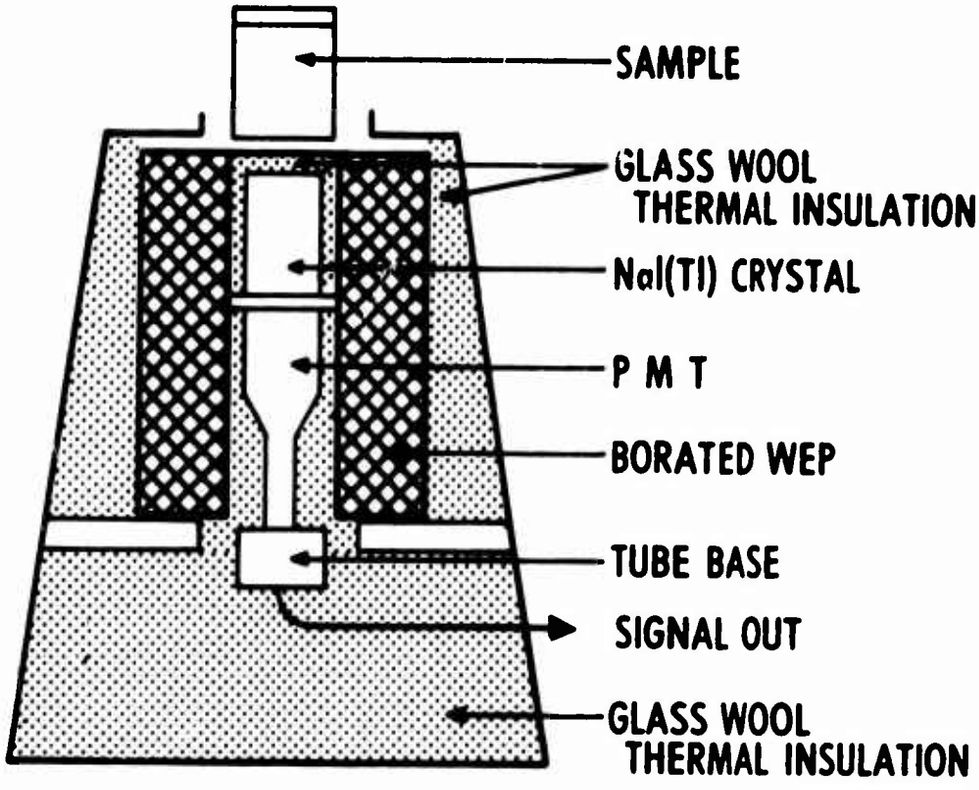


Figure 4. Detector system for determination of cement content in plastic cement, soil-cement mixture, and standard core samples.

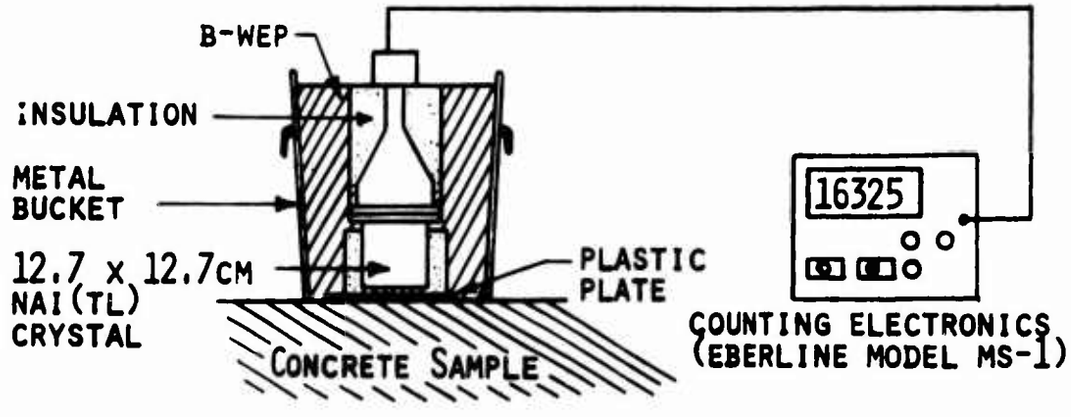


Figure 5. Diagram of the detector system used for the determination of cement content "in-place" concrete.

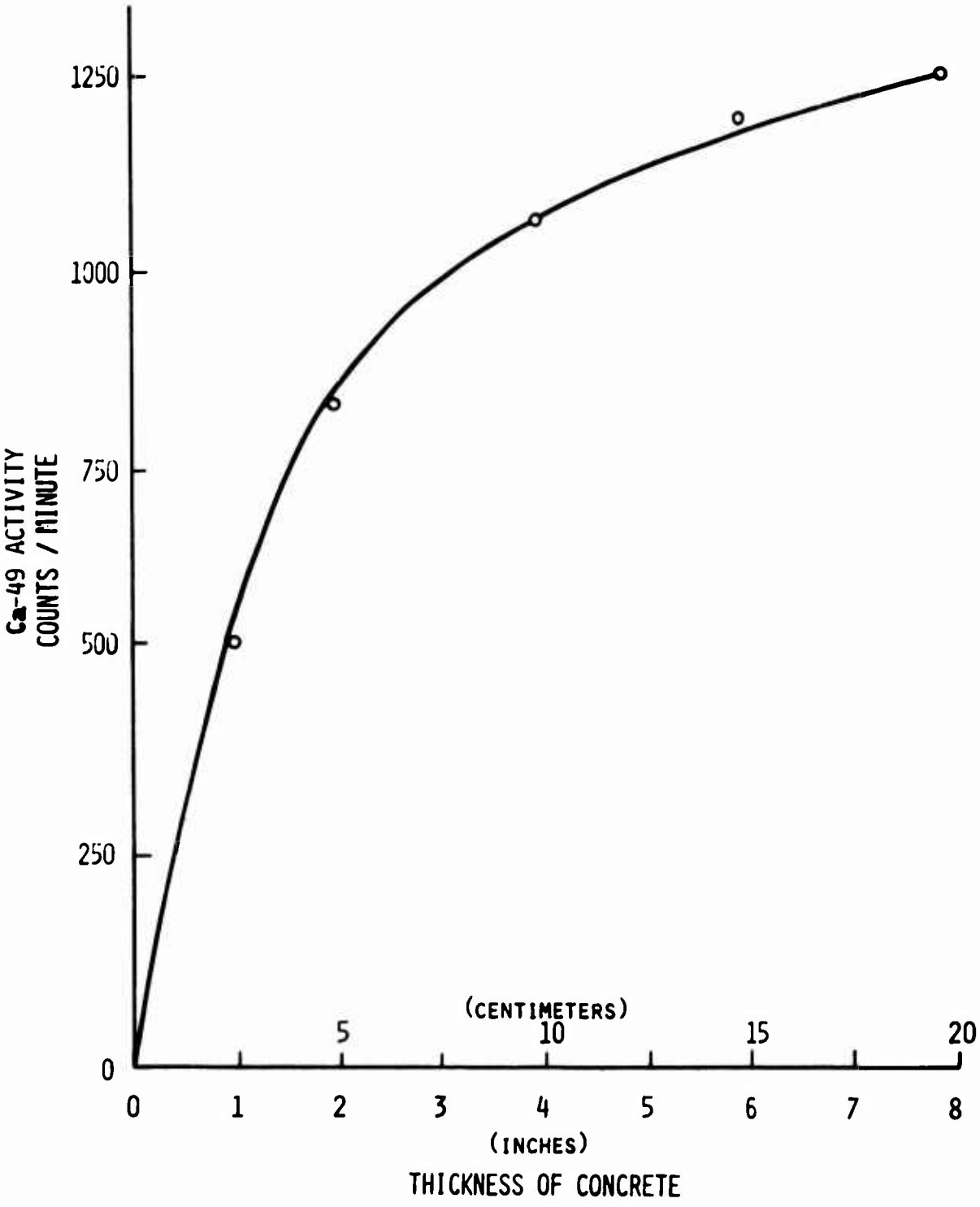


Figure 6. Thickness of a concrete sample that produces useful information on cement content.

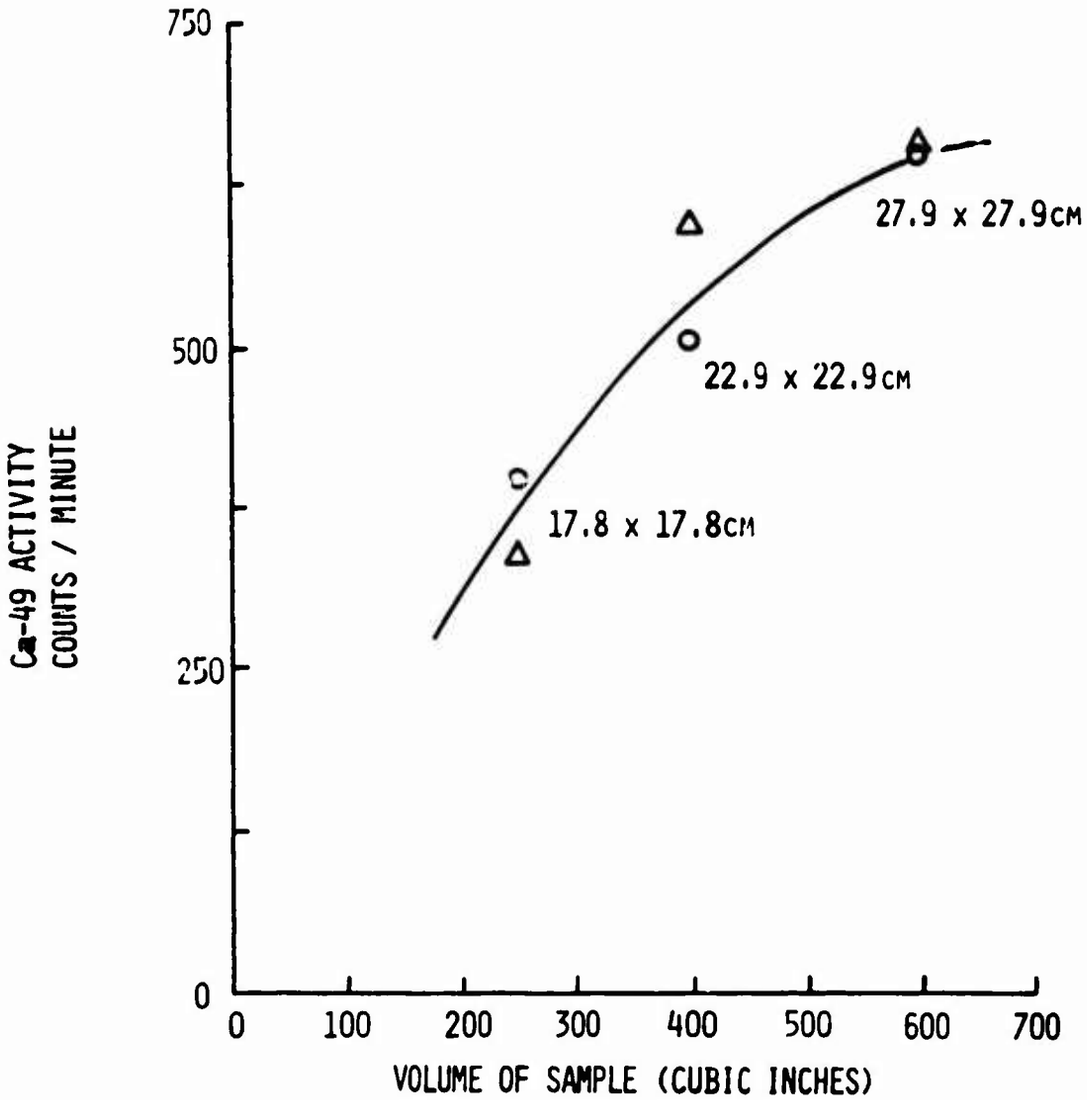
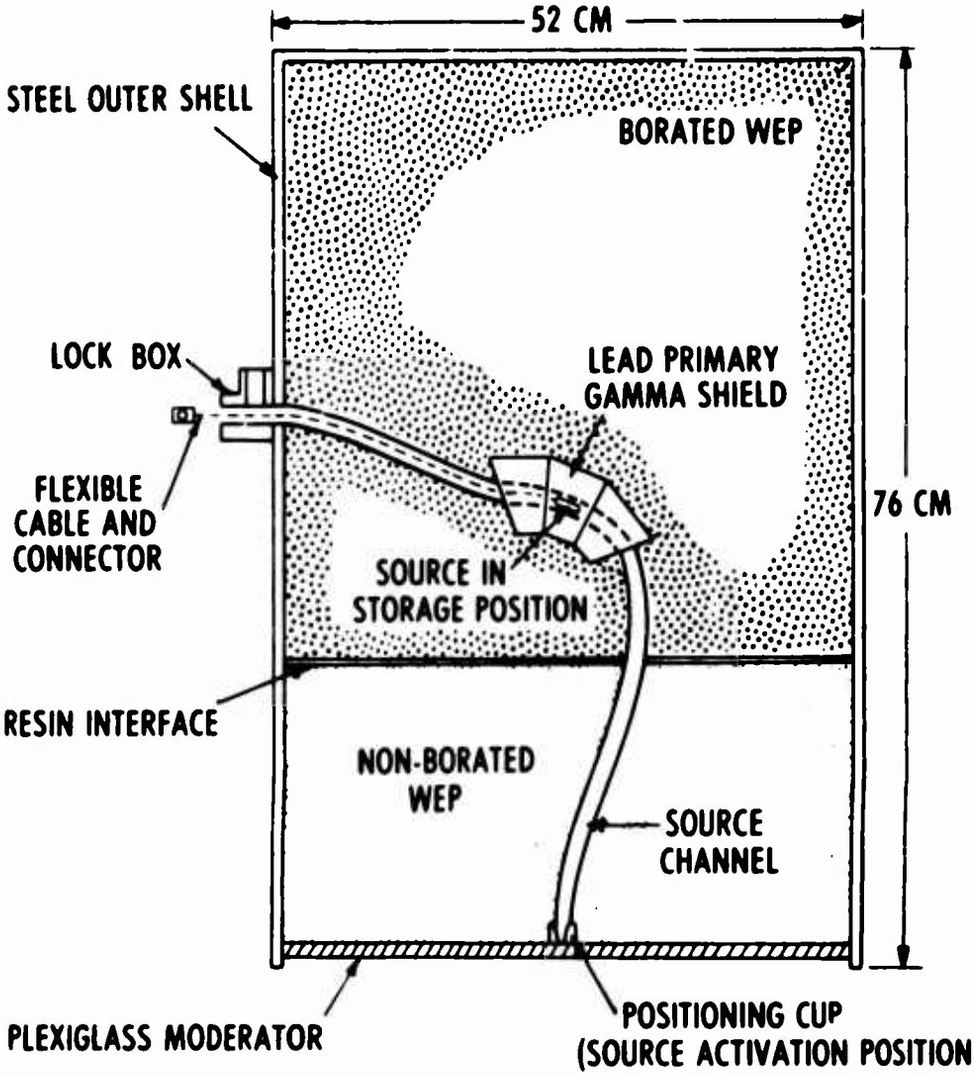


Figure 7. Increase in cement content signal with sample size for concrete slabs 12.7 cm (thick).



WEP - 60% WATER AND 40% RESIN (ASHLAND CHEMICAL CO., COLUMBUS OHIO).

Figure 8. Cross-sectional diagram of activation shield assembly for analysis of "in-place" concrete.

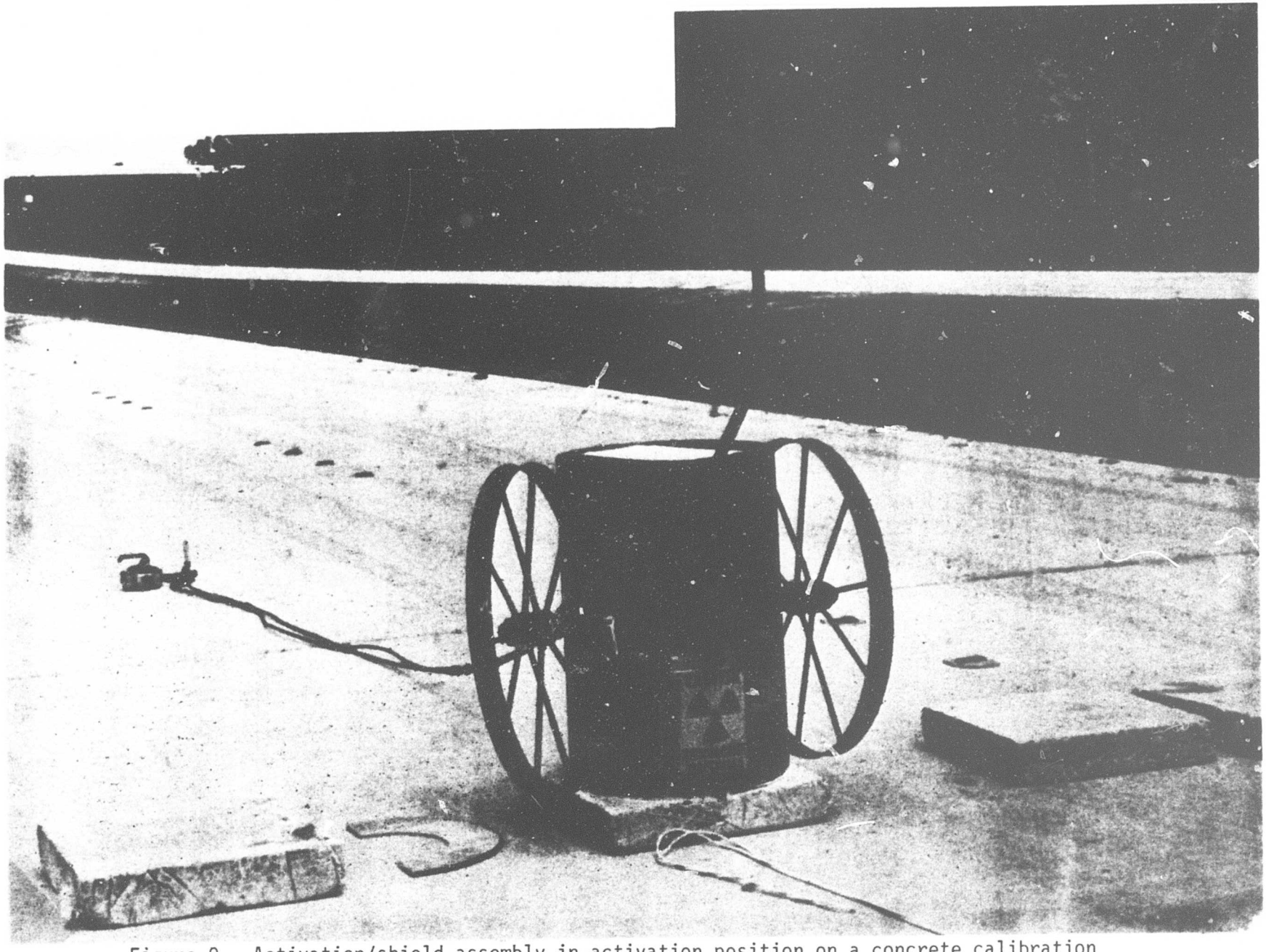


Figure 9. Activation/shield assembly in activation position on a concrete calibration slab (remote crankout and cable are visible behind the assembly).

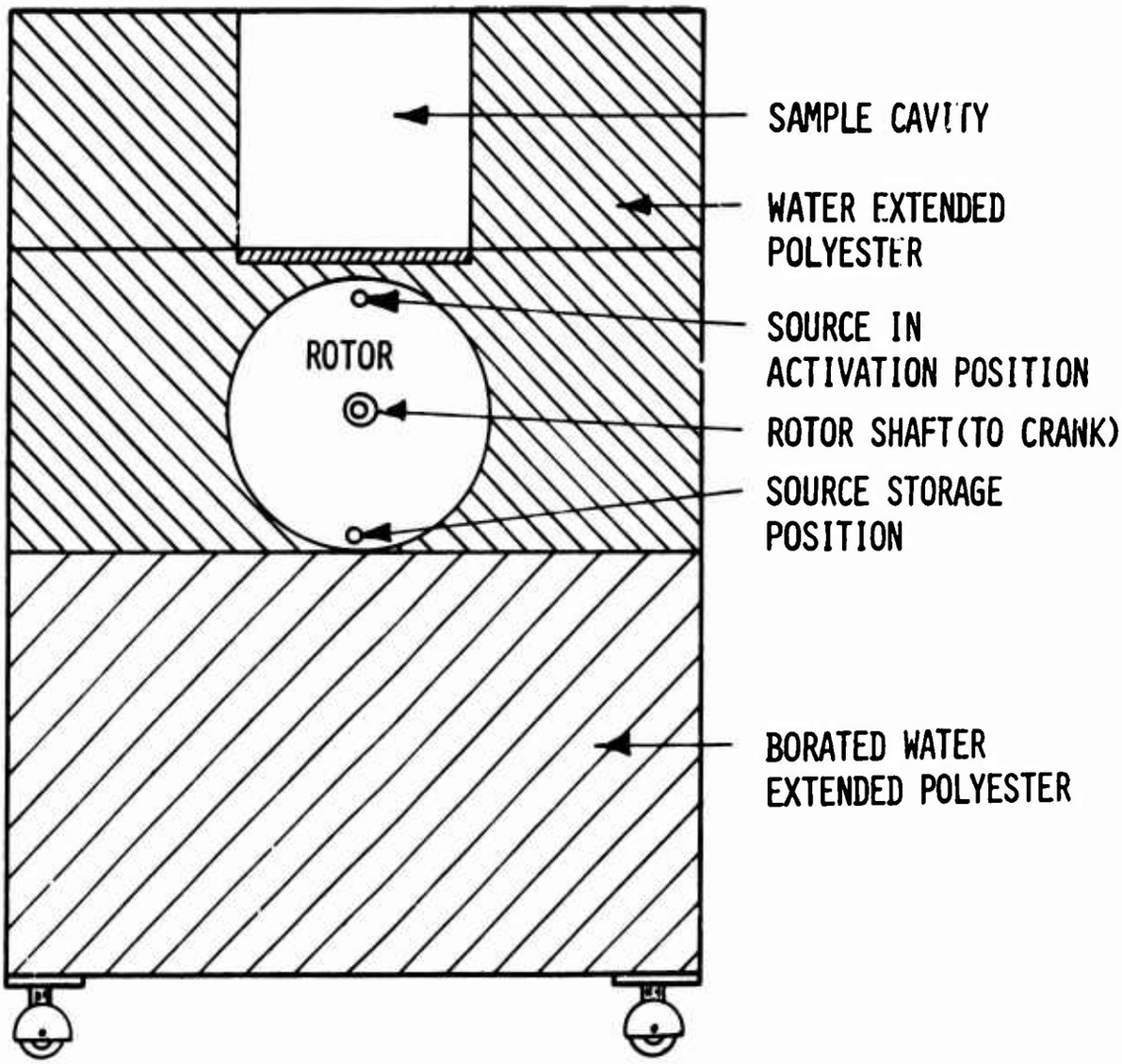


Figure 10. Activation/shield assembly for use with plastic concrete samples (cross-sectional view).

PRELIMINARY EVALUATION OF THE NEUTRON-GAMMA TECHNIQUE TO DETERMINE THE WATER AND CEMENT CONTENT OF FRESH CONCRETE

by

Paul A. Howdyshell

Civil Engineer
Construction Engineering Research Laboratory

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ABSTRACT

This paper describes a multiple signature concept for determining the water and cement contents of fresh concrete. It presents the equipment and test techniques devised for determining signature intensities and describes the initial evaluation of the system.

The multiple signature concept is based upon the relation of signature intensities to chemical element intensities. Since concrete consists of four constituents (water, cement, fine aggregates, and coarse aggregates), four signature elements are required. The elements selected for evaluation are H, Ca, Si, and C.

A prototype neutron-gamma system has been developed that can obtain signatures on the H, Ca, Si, and C present in fresh concrete. An evaluation of the unit using mortar mixes indicates that the unit is accurate to 1 to 1.5 percent for the H, Ca, and Si signatures, and to 2 to 3.0 percent for the C signature. The mortar tests also indicated that the Ca, Si, and C signatures were sensitive to the level of hydrogen (water) present in the sample being tested; however, the sensitivity was negligible for water variations normal to concrete. The results indicated some Ca interference in the computation of the H signature, but it was concluded that this could probably be overcome by computation modifications.

Further evaluation of the neutron-gamma unit is needed before its complete capabilities are understood.

PRELIMINARY EVALUATION OF THE NEUTRON-GAMMA TECHNIQUE TO DETERMINE THE WATER AND CEMENT CONTENT OF FRESH CONCRETE

by

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INTRODUCTION

Background

Most nuclear systems that have been developed for determining water and/or cement contents of fresh concrete rely on single signatures. The common deficiency of single signature systems is their lack of uniqueness to the cement or water contents of fresh concrete; thus, variables other than cement and water can influence the signature's intensity.

Purpose

This paper describes a new multiple signature concept for determining water and cement contents of fresh concrete. It presents the equipment and test technique devised for determining signature intensities and gives an initial evaluation of the system.

THE MULTIPLE SIGNATURE CONCEPT

The multiple signature concept is based upon having a relationship between each signature intensity and a chemical element intensity. The principle of the signature element technique is related to the solution of linear simultaneous equations of the following form:

$$N_i = \Sigma_j k_{ij} C_j \qquad \text{[Eq 1]}$$

where N_i = concentration of signature element "i" in the mix

C_j = concentration of constituent "j" in the mix

k_{ij} = concentration of signature element "i" in constituent "j".

To determine constituent material proportions, the number of signature elements must equal (or exceed) the number of chemically unique

constituents, and each constituent must contain at least one signature element.

Signature element selection is dictated by: (1) the requirements of equation 1, and (2) the elements having some type or form of detectable nuclear signature.

Early studies by Iddings had considered the idea of using neutron activation analysis to obtain calcium and silicon signatures on concretes. The relevant reactions were $^{48}Ca(n, \gamma)^{49}$ Ca, half-life 8.8 minutes, gamma energy 3.1 MeV; and $^{28}Si(n,p)^{28}Al$ and $^{27}Al(n,\gamma)^{28}Al$, half-life 2.3 minutes, gamma energy 1.78 MeV.[1]

It is well known that conventional nuclear moisture-density gauges rely on the neutron attenuation characteristics of hydrogen for their moisture signatures.[2] Thus, current technolgoy indicates that three elements common to concrete (hydrogen, calcium, and silicon) exhibit some type of detectable nuclear signature. However, since most concretes are comprised of four chemically distinct constituents (water, cement, coarse aggregates, and fine aggregates), another signature element is needed to satisfy the requirements of the mathematical solution.

An investigation of the chemical composition of concrete constituents indicates that carbon is an excellent signature element. When comparing the chemical compositions of calcareous aggregates and cements, carbon is found to be unique to the aggregate, and thus provides a ready means of distinguishing between the calcium contributed by the cement and the calcium contributed by the calcareous aggregates.

A contract was awarded to Columbia Scientific Industries in 1972 to evaluate the feasibility of obtaining neutron-gamma signatures on the hydrogen (H), calcium (Ca), silicon (Si), and carbon (C) present in fresh concrete. Results of the study indicate that no single neutron source technique is capable of determining all four primary signature elements (H, C, Si, and Ca) for fresh concrete, but that it is possible to meet the requirement by using a combination of techniques.[3] Table 1 is a summary and an evaluation of the various neutron-gamma techniques evaluated. The table indicates that two sources (Cf-252 and Pu-Be), with NaI detectors set up to monitor both prompt and delayed gammas,

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[1] Frank Iddings, et al, *Nuclear Techniques for Cement Determination* (Louisiana State University, April 1968).

[2] J Bharagava, "Application of Some Nuclear and Radiographic Methods on Concrete," *Matereaus Et Construction*, Vol 4, No. 22 (1971) pp 231-260.

[3] M. C. Taylor, *A New Method for Field Analysis of Plastic Concrete--Feasibility Study*, Technical Report M-64 (Construction Engineering Research Laboratory [CERL], December 1973).

provide the most effective means of measuring the H, C, Si, and Ca contents of fresh concrete.

NEUTRON-GAMMA PROTOTYPE INSTRUMENT

The prototype neutron-gamma instrument is based upon results of the feasibility study. The instrument package is designed around two isotope sources and three NaI (Tl) gamma ray spectrometers. The system performs four basic neutron-gamma analytical functions, either individually or in various combinations. These four basic analyses are:

(1) Prompt gamma analysis with thermalized neutrons from a Cf-252 source

(2) Activation analysis with thermalized neutrons from a Cf-252 source

(3) Prompt gamma analysis with fast neutrons from a Pu-Be source

(4) Activation analysis with fast neutrons from a Pu-Be source.

Equipment

The equipment consists of a thermal neutron cell (TNC), a fast neutron cell (FNC), an activation counting cell (ACC), and a control unit. The TNC unit (Figure 1) consists of a Cf-252 source (250 to 150μg) mounted on an 18-in. diameter rotating wheel, a motor and clutch system for driving the wheel, a 5 in. x 5 in. NaI (Tl) detector and preamp, and a junction box for interfacing to the control unit. The system is shielded in a 32-in. diameter steel cylinder filled with a borated-water extended polyester resin (WEP). Source-detector shielding consists of lead, tungsten, and lithium hydride. There is a 1 3/4-in. lucite moderator between the source and the sample.

The FNC unit (Figure 2) is similar to the TNC unit, but has an unmoderated 37-curie Pu-Be source mounted on a 15-in. rotating wheel housed in a WEP-filled, 24-in. diameter steel cylinder.

The activation counting cell (Figure 3) consists of a 5 in. x 5 in. NaI (Tl) detector and has a preamp and junction box for interfacing to the control unit. The detector is shielded by lead rings in a 24-in. diameter, WEP-filled steel cylinder.

The electronic control unit (Figure 4) consists of a 1024 channel analyzer, a high voltage power supply, three linear amplifiers, a mixer/-

router module, a control module, and a powered NIM* bin.

Operating Procedures

The equipment is operated by transmitting signals from each of the three detector systems to one of three amplifiers in the control unit. The output pulses are then sent to the mixer/router module, which directs them to a specific 256-channel memory group (one of four available) in the multichannel analyzer. Each input to the mixer/router has a corresponding gate input from the control module; thus, the analyzer accumulates a particular signal only during the period of time when its gate is open. Each gate is open for a period specified by its present-time on the control module. Elemental concentrations are proportional to the area under corresponding peaks in the multichannel analyzer spectrum.

Figure 5 is a flow diagram of the analysis procedure as it is used for analyzing concrete samples. The figure illustrates which signature elements are associated with each of the three units. The standard test sequence used is:

(1) Using 2-gal paint pails as sample containers, place a 10-kg concrete sample on the TNC unit and one on the FNC unit.

(2) Start irradiation and counting (5 min for the TNC cell, and 10 min for the FNC cell).

(3) After completing the 5 min of TNC irradiation and counting, transfer the TNC sample to the activation counting cell. (One min is allowed for the transfer.)

(4) After the 1-min delay, the activation cell counts for 5 min.

(5) The run is completed in 11 min.

After the run has been completed, the analyzer's collect function is switched off, and the collected gamma spectra from each of the three detectors can be displayed for scope analysis. The analyzer also digitalizes the collected data on a per channel, per event basis. The unit can sum or integrate the intensities of any consecutive group of channels.

LABORATORY TESTS

The initial laboratory test series on the prototype unit consisted

* Nuclear Instrumentation Module (AEC standard).

of running the standard neutron-gamma tests on various mortar mixes and their constituents.

The mortar tests evaluated three different aggregates, three sand/cement ratios, and nine water contents. Standard ottawa sand, river sand, and crushed limestone were the aggregates tested. The sand/cement ratios were 3 to 1, 4 to 1, and 6 to 1. The mix water varied from a low of 7.5 percent to a high of 10.8 percent. Table 2 lists the mix designs used for the entire test series.

The test procedure included weighing out the mix constituents and obtaining a 1-kg sand sample for moisture determination. The batches, weighing approximately 60 lb each, were mixed in a 1-cu ft capacity laboratory bowl mixer. After mix homogeneity had been obtained, two 10-kg samples were placed in the 2-gal paint pails. The standard neutron-gamma test was conducted on the sample. Standard neutron-gamma tests were also conducted on the cement, ottawa sand, river sand, and crushed limestone used to make the mortar mixes.

After completion of the irradiation-counting cycle for each neutron-gamma test, the TNC spectrum was analyzed for the 2.22 MeV gamma rays from the H(N, γ)D neutron capture reaction. The FNC spectrum was analyzed for the 4.43 and 1.78 MeV gamma rays from the $^{12}C(n,n')^{12}$ and the $^{29}Si(n,n')^{28}Si$ neutron inelastic scattering reactions respectively. The spectrum from the ACC unit was analyzed for the 3.09 MeV gamma rays from the $^{48}Ca(n,\gamma)^{49}Ca$ neutron activation reaction, and for the 1.78 MeV gamma rays from both the $^{27}Al(n,\gamma)^{28}Al$ and the $^{28}Si(n,p)^{28}Al$ reactions.

Spectrum analysis involved determination of the net peak intensities for the five gamma energies listed above. This was accomplished by subtracting background intensities from peak intensities. For calculating peak intensities, all peaks were assumed to be a band eight channels wide. Background intensities were computed by skipping one channel and counting the next four on both sides of the eight-channel peak band. The exception to this procedure was the 2.22 MeV H signature; it used a six-channel peak band with three channel backgrounds.

Since there was some drift in the location of the peak channels, net peak intensities were computed for an entire series of band locations. This continued until the maximum net peaks and the net peaks for bands starting one channel on either side had been obtained. The maximum net peak intensities were the only ones used in the data analysis.

Tables 3, 4, and 5 list the signature (net peak) intensities obtained respectively for the ottawa sand, river sand, and crushed limestone mortar tests. Table 6 contains signature intensities obtained from tests of the mortar constituents.

DISCUSSION AND ANALYSIS OF LABORATORY TESTS

When analyzing the mortar tests data, the signature intensities of the individual constituents cannot be used to estimate the peak intensities of the various mortar mixes. The Ca and Al-Si signatures from activation analysis are much higher for the mortars than for the individual constituents. The reverse is true for the Si and C signatures from inelastic scattering. The most probable reason for this is the presence of hydrogen in the form of water in the mortar mixes. Hydrogen is an excellent neutron moderator, and increased hydrogen content increases the tendency for neutron moderation. Thus, nuclear reactions that occur only when thermalized neutrons* are present, will become more intense in an increased hydrogen environment. The most prominent example is the $^{48}CA(n,\gamma)^{49}Ca$ neutron activation reaction, which only occurs with thermal neutrons. The reverse is true for reactions that require neutron energies above a specific threshold value, e.g., the inelastic scattering reactions. Neutron energies must be above the characteristic gammas produced for inelastic scattering to occur. Thus, neutrons that have moderated below 4.43 MeV cannot scatter inelastically with carbon. This is also true of the neutron below 1.78 MeV and of silicon.

To further evaluate the matrix effects of hydrogen (water) on the other signatures, the ottawa sand mortar test series was evaluated by a moving average technique. Each point of the moving average was the mean value of the signature intensities for three consecutive mixes of increasing water content. Figures 6 through 9 are graphs of cement contents versus moving average net peaks for the Si, C, Ca, and Al-Si signatures.

The spread of data points for the C and Ca signatures (Figures 7 and 8) is not significantly greater than their related counting error.** This indicates that for the hydrogen range tested (water contents varying from 7.5 to 10.8 percent), the influence on the C and Ca signatures is negligible when compared to the theoretical accuracy of the equipment. The results obtained for the Al-Si signature (Figure 9) are more varied, but not specific trends relative to changes in water content were observed. The results obtained for the Si signature are considerably different (Figure 6). As indicated earlier, increased hydrogen

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* Thermalized neutrons are neutrons moving at natural resonance velocity.

** All nuclear events are random in character. If two successive readings are taken by a counter exposed to a constant source of ionizing particles, the results will probably differ somewhat. This is defined as the statistical error of the counter. In standard deviation units (σ) an approximation of this is $\sigma\sqrt{n}$, where n equals the total count taken. In the presence of background activity, the equation becomes $\sigma\sqrt{n_p + n_b}$, where n_p = total peak count and n_b = background count.

content decreases the intensity of the Si signature. However, even for the Si signature, the sensitivity is small, and a 32 percent change in hydrogen content decreases the intensity of the silicon signature by only 4.2 percent.

For each sand type (ottawa sand, river sand, and crushed limestone), the Si, C, Ca, and Al-Si signatures (net peaks) were averaged per sand/cement ratio. Figures 10, 11, 12, and 13 depict these averages plotted against cement content. It can be noted from the figures that most of the signature intensities are linearly related to cement content. In those cases where linearity is not observed, it is suspected that variations in aggregate moisture content which were not corrected is the major influencing factor. This is particularly true for the river sands which had aggregate moisture contents as high as 5 and 6 percent.

Figure 14 is a plot of the water contents of all the mixes versus the H signature. The figure indicates that there are large differences in the hydrogen signatures of a given water content for each of the sands tested. An analysis of the gamma spectrum indicated that a 1.94 MeV Ca full escape peak was interfering with the background channels of the 2.22 MeV gammas from the H full escape peak. Thus, for a given water content, higher Ca contents produce smaller net H signature intensities. It is assumed that the majority, if not all of this problem, could be resolved by decreasing the width of the peak channels from 6 to 4.

Analysis of the test data also indicated that the carbon signature associated with the ottawa sand, cement, and ottawa sand/cement mortar mixes must be background carbon from the source shielding material, since no appreciable level of carbon is present in either constituent (Figure 7, Tables 3 and 6). Table 6 also indicated that the Al-Si signature is more sensitive to variations in Al than to variations in Si content. This is proven by the higher signature intensity for cement (approximately 21 percent SiO_2 and 6 percent Al_2O_3) than for ottawa sand (approximately 100 percent SiO_2).

In an attempt to determine the accuracy of the prototype equipment and to understand the chemical uniformity of the mortar constituents, the counting errors for the various signatures were compared to the sampling errors for the six cement, ottawa panel, river sand, and limestone samples tested. The results (Table 7) indicate that the counting statistics for the Si, Al-Si, and Ca signatures are small. The counting statistics for the C signature are larger, but comprise only about 2 percent for the limestone samples. In all cases, the sampling errors were considerably larger than the counting errors. Some difference was expected but not as much as the amount that occurred. One possible cause of the nonuniformity was the lack of uniform control over the samples' moisture contents; in addition, as indicated previously, the presence of hydrogen can signficantly alter peak intensities.

SUMMARY AND CONCLUSIONS

A multiple signature concept has been devised to determine the water and cement contents of fresh concrete. The concept is based upon the relation of signature intensities to chemical element intensities. Four signature elements are required. The elements selected for consideration were H, Ca, Si, and C.

A prototype neutron-gamma unit that can obtain signatures on the H, Si, Ca, and C present in fresh concrete has been developed. The tests made by this unit require 11 minutes to complete. The accuracy (counting error) of the unit is .5 to 2.0 percent for the H, Ca, and Si signatures, and 2 to 4 percent for the C signature.

The mortar test series indicated that the Si (both the inelastic Si signature and the Al-Si activation signature), Ca, and C signatures are sensitive to the presence of H in a sample; however, within the water content variations normally found in concretes, this sensitivity is negligible or very small.

The mortar tests also indicated that the H signature background channels were overriding a Ca related peak, thus allowing the Ca content of the sample to interfere with the background count of the H signature. This can readily be resolved by decreasing the width of the H peak.

Tests on the mortar constituents indicated that signatures obtained from constituent tests cannot be used to estimate the signatures for the mortar mixes due to the drastic difference in matrix composition (presence of water). Thus, there is still a need for some type of constituent calibration technique.

REFERENCES

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Iddings, Frank, et al, *Nuclear Techniques for Cement Determination* (Louisiana State University, April 1969).

Taylor, M. C., *A New Method for Field Analysis of Plastic Concrete--Feasibility Study*, Technical Report M-64 (Construction Engineering Research Laboratory [CERL], December 1973).

Table 1

Summary of Neutron-Gamma Mehods for Concrete Analysis

Element	Importance	Technique	Reaction	Source	Detector	Gamma Energy (MeV)	Comments
Hydrogen	Primary	Thermal neutron capture	H(n,.)D	^{252}Cf	NaI(Tl)	2.22	Best method
					Ge(Li)	2.22	Better resolution, but less sensitive and more expensive
		Fast neutron capture	H(n,.)D	Pu-Be	NaI(Tl)	2.22	Less sensitive than thermal capture
				14 MeV	NaI(Tl)	2.22	Least sensitive method
Carbon	Primary	Thermal neutron capture	$^{12}C(n,.)^{13}C$	^{252}Cf	Ge(Li)	4.95	Very low intensity
		Neutron inelastic scattering	$^{12}C(n,n')^{12}C$	^{252}Cf	NaI(Tl)	4.43	Very low intensity due to source spectrum
				Pu-Be	NaI(Tl)	4.43	Best method provided source is well shielded
					Ge(Li)	4.43	Offers no advantage due to Doppler broadening of gamma peak
				14 MeV	NaI(Tl)	4.43	Interference from $^{16}O(n,n'\alpha)^{12}C$ for n energies $\geq$ 12.5 MeV

Table 1 (cont'd)

Element	Importance	Technique	Reaction	Source	Detector	Gamma Energy (MeV)	Comments
Silicon	Primary	Thermal neutron capture	$^{28}Si(n,\gamma)^{29}Si$	^{252}Cf	Ge(Li)	3.53	Requires large expensive source
		Neutron activation	$^{28}Si(n,p)^{28}Al$	^{252}Cf	NaI(Tl)	1.78	Works well with source unmoderated
				Pu-Be	NaI(Tl)	1.78	Works very well - $\sim$ 0.1 percent precision
				14 MeV	NaI(Tl)	1.78	Works very well - $\sim$ 0.1 percent precision
		Neutron inelastic scattering	$^{28}Si(n,n')^{28}Si$	Pu-Be	NaI(Tl)	1.78	Works reasonably well
				14 MeV	NaI(Tl)	1.78	Works reasonably well
Calcium	Primary	Thermal neutron capture	$^{40}Ca(n,\gamma)^{41}Ca$	^{252}Cf	Ge(Li)	6.42	Requires large expensive source
		Neutron activation	$^{48}Ca(n,\gamma)^{49}Ca$	^{252}Cf	NaI(Tl)	3.09	Works well
Aluminum	Secondary	Activation analysis	$^{27}Al(n,\gamma)^{28}Al$	^{252}Cf	NaI(Tl)	1.78	Requires well moderated source
			$^{27}Al(n,p)^{27}Mg$	Pu-Be or 14 MeV	NaI(Tl)	0.84	Can have interference from iron

Table 1 (cont'd)

Element	Importance	Technique	Reaction	Sour :	Detector	Gamma Energy (MeV)	Comments
Magnesium	Secondary	Activation analysis	$^{24}Mg(n,p)^{24}Na$	Pu-Be or 14 MeV	NaI(Tl)	2.75	Works reasonably well
Iron	Secondary	Activation analysis	$^{56}Fe(n,p)^{56}Mn$	Pu-Be or 14 MeV	NaI(Tl)	0.85	May require delay before count to avoid aluminum interference

Table 2

Mortar Test - Mix Proportions

(percent by wt)

	Batch No.	1-A	1-B	1-C	1-D	1-E	1-F	1-G	1-H	1-I
High cement	Water	7.50	7.90	8.35	8.73	9.10	9.55	9.98	10.40	10.80
Content series	Cement	23.1	23.0	22.9	22.8	22.7	22.6	22.5	22.4	22.2
(3 to 1 sand/cement ratio)	Sand	69.5	69.0	68.8	68.4	68.1	67.9	67.5	67.2	67.0
	Batch No.	2-A	2-B	2-C	2-D	2-E	2-F	2-G	2-H	2-I
Medium cement	Water	7.50	7.90	8.35	8.73	9.10	9.55	9.98	10.4	10.8
Content series	Cement	18.5	18.4	18.3	18.3	18.2	18.1	18.00	17.9	17.8
(4 to 1 sand/cement ratio)	Sand	74.0	73.7	73.3	73.0	72.7	72.4	72.0	71.7	71.4
	Batch No.	3-A	3-B	3-C	3-D	3-E	3-F	3-G	3-H	3-I
Low cement	Water	7.50	7.90	8.35	8.73	9.10	9.55	9.98	10.4	10.8
Content series	Cement	13.2	13.2	13.1	13.1	13.0	12.9	12.9	12.8	12.8
(6 to 1 sand/cement ratio)	Sand	79.3	79.0	78.6	78.3	77.9	77.5	77.2	76.8	76.5

Table 3

Laboratory Tests - Mortar Mixes

Ottawa Sand-Cement
Element Signature Intensities

6 to 1 Sand/Cement Ratio

Mix Proportions			H	Si	C	Ca	Al-Si
Water	Cement	Sand	(TNC)	(FNC)	(FNC)	(ACC)	(ACC)
7.50	13.24	79.26	41,583	361,100	14,175	2,495	99,658
7.90	13.18	78.92	49,219	358,496	14,584	2,119	96,409
8.35	13.12	78.53	51,927	351,745	13,247	2,462	103,056
8.73	13.06	78.21	54,541	351,931	13,733	2,102	96,386
9.10	13.00	77.90	55,120	353,533	14,280	2,068	93,010
9.55	12.94	77.51	60,271	351,542	14,041	2,068	93,820
9.98	12.88	77.14	70,052	344,653	12,491	2,379	98,203
10.40	12.82	76.78	68,840	341,436	13,904	2,555	99,040
10.80	12.76	76.44	71,444	338,323	14,484	2,426	92,050
			x	350,307	13,882	2,297	97,403
			Sx	7,537	660	203	3,054
			C.V.	2.1	4.8	8.8	3.1

4 to 1 Sand/Cement Ratio

7.50	18.51	73.99	40,547	341,425	14,010	3,200	109,204
7.90	18.42	73.68	43,231	342,750	13,255	3,298	111,098
8.35	18.33	73.32	48,324	337,766	13,405	3,559	113,944
8.73	18.25	73.02	51,222	335,930	13,268	3,293	113,238
9.10	18.20	72.70	55,503	339,668	13,480	3,406	116,125
9.55	18.10	72.35	58,117	332,093	12,775	3,583	115,681
9.98	18.00	72.02	62,008	327,241	13,433	3,512	113,845
10.40	17.92	71.68	62,925	321,126	13,158	3,494	111,786
10.80	17.84	71.36	66,712	319,106	14,333	3,581	112,584
			x	333,012	13,457	3,436	113,056
			Sx	8,730	462	143	2,187
			C.V.	2.6	3.4	4.16	1.9

3 to 1 Sand/Cement Ratio

7.50	23.10	69.40	39,266	335,240	13,571	4,012	119,147
7.90	23.00	69.10	40,970	329,175	14,022	4,092	120,627
8.35	22.90	68.75	46,886	322,007	13,442	4,344	128,407
8.73	22.80	68.47	51,799	321,020	14,970	4,593	131,705
9.10	22.70	68.20	51,753	319,322	12,994	4,573	127,448
9.55	22.60	67.85	60,020	320,623	13,784	4,436	131,277
9.98	22.50	67.52	61,390	313,940	13,250	4,502	127,571
10.40	22.40	67.20	64,989	313,273	13,323	4,614	126,585
10.80	22.20	67.00	66,096	309,466	13,548	4,584	124,305
			x	320,452	13,656	4,417	126,341
			Sx	8,011	576	224	4,312
			C.V.	2.5	4.2	5.1	3.4

Table 4

Laboratory Tests - Mortar Mixes

River Sand-Cement
Element Signature Intensities

6 to 1 Sand/Cement Ratio

Mix Proportions			H	Si	C	Ca	Al-Si
Water	Cement	Sand	(TNC)	(FNC)	(FNC)	(ACC)	(ACC)
11.02	13.24	75.74	66,060	269,095	15,499	3,622	212,071
10.81	13.18	76.01	65,908	266,396	15,492	3,666	207,721
11.25	13.12	75.63	72,729	268,479	13,229	3,696	221,709
12.25	13.06	74.69	75,815	259,740	15,618	3,631	213,497
11.10	13.00	75.90	65,319	263,400	16,715	4,327	247,251
11.48	12.94	75.58	69,370	258,913	15,030	3,699	184,822
13.56	12.88	73.56	96,111	254,370	14,745	3,677	223,384
14.54	12.82	72.64	94,294	254,209	16,207	4,036	229,416
14.60	12.76	72.64	92,751	247,777	16,745	3,783	214,506
			x	260,264	15,475	3,793	217,153
			Sx	7,265	1,088	237	16,942
			C.V.	2.8	7.0	6.2	7.8

4 to 1 Sand/Cement Ratio

9.27	18.51	72.22	49,170	260,639	15,264	5,532	254,206
9.96	18.42	71.62	54,394	258,169	15,216	5,360	257,507
10.65	18.33	71.01	61,971	252,641	14,475	5,532	262,215
11.29	18.25	70.46	65,877	246,233	15,529	5,624	259,842
10.77	18.20	71.03	62,193	261,266	15,985	5,364	254,716
11.45	18.10	70.45	67,289	253,991	16,510	5,505	260,104
11.81	18.00	70.19	72,894	249,376	15,090	5,888	274,290
12.37	17.92	69.71	77,606	248,144	14,617	5,735	274,879
13.12	17.84	69.04	78,407	242,420	17,142	5,778	265,789
			x	252,542	15,536	5,591	262,616
			Sx	6,586	822	183	7,665
			C.V.	2.6	5.3	3.3	2.9

3 to 1 Sand/Cement Ratio

9.04	23.10	67.86	46,801	255,893	15,100	6,174	259,540
9.41	23.00	67.59	52,259	255,073	12,507	6,341	277,077
10.31	22.90	66.79	53,937	240,375	14,195	6,276	256,518
10.78	22.80	66.42	56,836	241,745	15,514	6,262	254,209
10.75	22.70	66.55	59,337	242,276	15,359	6,323	259,019
11.36	22.60	66.04	62,229	239,085	15,099	6,545	256,867
11.86	22.50	65.64	66,379	237,059	12,356	6,155	263,181
12.44	22.40	65.16	71,295	233,155	15,076	6,707	267,765
12.81	22.20	64.99	72,665	232,879	16,985	6,578	263,662
			x	241,948	14,687	6,373	261,982
			Sx	8,374	1,472	181	7,042
			C.V.	3.5	10.0	2.8	2.7

Table 5

Laboratory Tests - Mortar Mixes

Crushed Limestone-Cement
Element Signature Intensities

6 to 1 Sand/Cement Ratio

Mix Proportions			H	Si	C	Ca	Al-Si
Water	Cement	Sand	(TNC)	(FNC)	(FNC)	(ACC)	(ACC)
8.18	13.24	78.58	28,195	80,242	26,546	13,938	62,240
8.74	13.18	78.08	31,686	83,456	24,869	14,528	67,306
9.21	13.12	77.67	36,388	83,590	25,529	14,703	71,297
9.60	13.06	77.34	35,691	79,737	24,959	14,821	68,363
9.25	13.00	77.75	30,110	67,740	26,722	15,312	58,262
9.64	12.94	77.42	34,518	69,972	27,184	15,146	58,238
10.83	12.88	76.29	46,750	83,419	25,800	15,079	70,292
11.31	12.82	75.87	44,700	83,678	27,465	14,710	68,886
11.61	12.76	75.63	52,429	81,884	25,980	14,886	66,084
			$\bar{x}$	79,302	26,117	14,791	65,662
			$S\bar{x}$	6,125	926	403	4,941
			C.V.	7.7%	3.5%	2.9%	7.5%

4 to 1 Sand/Cement Ratio

7.95	18.51	73.54	21,913	87,215	24,470	13,018	69,193
8.72	18.42	72.86	30,719	86,664	24,181	15,556	83,448
9.13	18.33	72.54	31,662	88,248	24,976	16,398	84,707
9.49	18.25	72.26	35,189	86,033	25,053	15,503	85,753
9.44	18.20	72.36	32,179	79,252	22,996	15,654	77,277
9.78	18.10	72.12	36,279	79,069	23,769	15,146	75,444
10.10	18.00	71.90	40,124	85,914	24,400	14,781	79,730
10.71	17.92	71.37	44,143	81,833	24,493	14,961	78,071
11.26	17.84	70.90	44,990	80,476	23,572	16,009	86,150
			$\bar{x}$	83,856	24,212	15,225	79,974
			$S\bar{x}$	3,658	667	968	5,631
			C.V.	4.4%	2.8%	6.4%	7.0%

3 to 1 Sand/Cement Ratio

8.54	23.10	68.36	30,070	94,292	22,565	13,913	86,068
9.14	23.00	67.86	31,720	97,489	23,280	14,601	96,936
9.75	22.90	67.35	34,239	89,823	22,247	11,180	66,148
10.21	22.80	66.99	40,364	92,175	23,595	13,440	90,819
9.48	22.70	67.82	36,357	88,343	23,970	14,933	89,642
9.73	22.60	6 .67	31,492	92,879	23,174	15,110	96,752
10.03	22.50	67.47	33,418	78,617	23,938	15,153	79,319
10.53	22.40	67.07	40,017	92,491	22.807	14,221	98,716
11.00	22.20	66.80	46,033	95,705	24,227	15,485	106,899
			$\bar{x}$	91,312	23,311	14,226	90,477
			$S\bar{x}$	5,513	680	1,316	11,926
			C.V.	6.0%	2.9%	9.2%	13.2%

Table 6

Laboratory Tests - Mortar Mix Constituents

Element Signature Intensities

Cement

Sample Moisture Content (%)		H	Si	C	Ca	Al-Si
Water	Dry Sample	(TNC)	(FNC)	(FNC)	(ACC)	(ACC)
	100	No	139,115	11,656	5,235	87,612
	100	H	136,169	8,154	4,842	79,989
	100	Peak	151,913	10,275	5,443	86,157
	100		152,638	11,272	4,731	77,173
	100		155,680	10,965	5,267	83,854
	100		150,840	10,269	6,058	95,067
$\bar{x}$			147,725	10,431	5,262	84,974
$S_{\bar{x}}$			8,029	1,243	474	6,281
C.V.			5.4	11.9	9.0	7.4

Ottawa Sand

	100	No	464,971	15,488	No	72,439
	100	H	486,620	14,926	Ca	57,125
	100	Peak	474,719	14,656	Peak	59,749
	100		476,869	13,977		44,782
	100		477,651	13,342		63,667
	100		480,639	14,048		58,305
$\bar{x}$			476,912	14,406		59,344
$S_{\bar{x}}$			7,157	767		9,039
C.V.			1.5	5.3		15.2

River Sand

2.51	97.48	14,826	346,993	17,924	1,142	162,583
5.03	94.97	27,950	332,845	17,032	798	119,274
4.86	95.14	23,440	337,154	17,086	1,103	146,724
4.24	95.76	24,472	333,126	15,936	973	142,378
7.18	92.82	40,443	326,536	16,873	975	141,377
2.96	97.04	15,827	347,097	16,807	857	130,814
$\bar{x}$ 4.46	95.54		337,292	16,943	965	140,525
$S_{\bar{x}}$ 1.67	1.67		8,283	636	136	14,663
C.V 37.5%	1.7%		2.5%	3.8	14.0%	10.4%

Crushed Limestone

0.11	99.89	No	73,560	33,250	5,269	12,602
0.00	100.00	H	70,761	31,691	5,935	11,675
0.93	99.07	Peak	83,130	26,828	7,133	22,114
0.86	99.14		84,925	33,299	6,778	22,589
1.61	98.39		93,908	30,253	6,920	25,462
0.78	99.22		91,810	29,970	6,777	29,180
$\bar{x}$ 0.72	99.28		83,150	30,881	6,468	20,603
$S_{\bar{x}}$ 0.59	0.59		9,372	2,438	715	7,030
C.V. 82%	0.6%		11.3%	7.9%	11.1%	34.1%

Table 7

Laboratory Tests - Mortar Mix Constituents

Uniformity of Signature Element Intensities
Counting Error Vs. Sampling Error

Constituents	Si			C			Ca			Al-Si		
	σ_c	$S\bar{x}$	Sx/σ_c	σ_c	Sx	Sx/σ_c	σ_c	$S\bar{x}$	Sx/σ_c	σ_c	$S\bar{x}$	Sx/σ_c
$S\bar{x}, \sigma_c$	1675	8029		639	1243		96	474		350	6281	
Cement			4.8			1.9			4.9			17.9
(%)C.V.	1.1	5.4		6.2	11.9		1.8	9.0		0.4	7.4	
$S\bar{x}, \sigma_c$	1865	7157		664	767					285	9039	
Ottawa Sand			3.8			1.2						31.8
(%)C.V.	0.4	1.5		4.7	5.3					0.5	15.2	
$S\bar{x}, \sigma_c$	1675	8283		630	636		59	136		426	14663	
River Sand			4.9			1.0			2.3			34.4
(%)C.V.	0.5	2.5		3.7	3.8		5.4	14		0.3	10.4	
$S\bar{x}, \sigma_c$	1638	9372		676	2438		98	715		202	7030	
Limestone			5.7	2.13		3.6			7.3			34.8
(%)C.V.	2.0	11.3			7.9		1.6	11.1		0.9	34.1	

NOTE: $\sigma_c = \sqrt{n_p + n_b}$

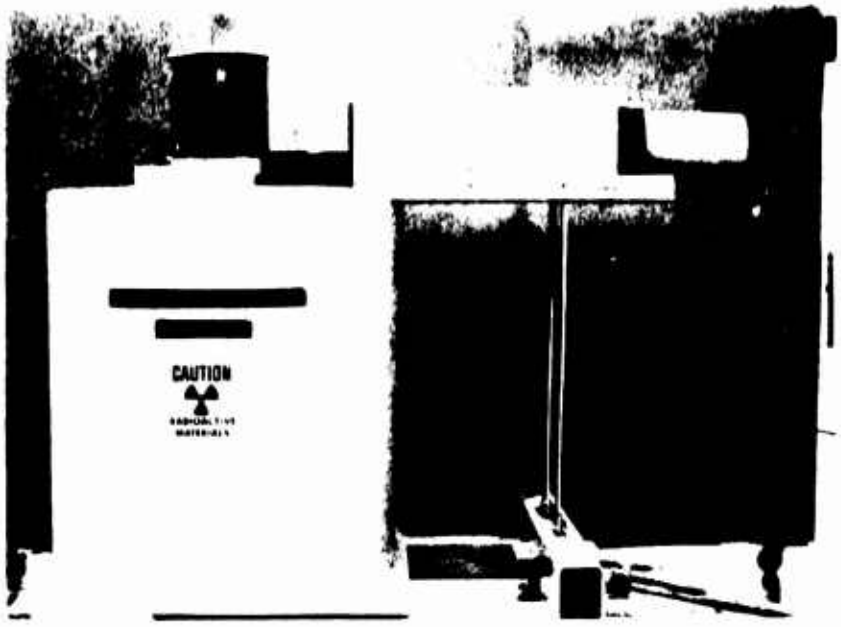
n_p = peak channel intensities

n_b = background channel intensities

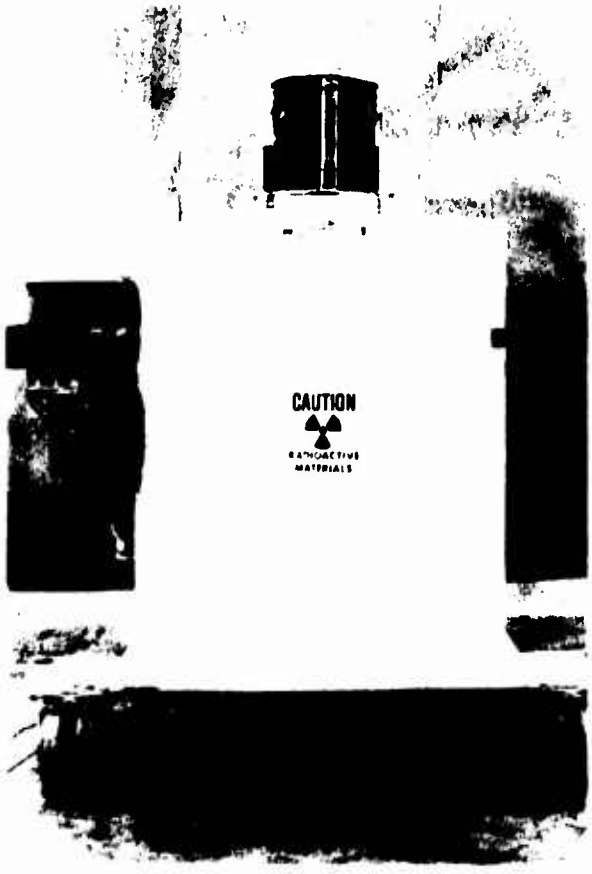
$$S\bar{x} = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n - 1}}$$

$\bar{x}$ = sample mean intensity (net peak)

x_i = net peak sample i

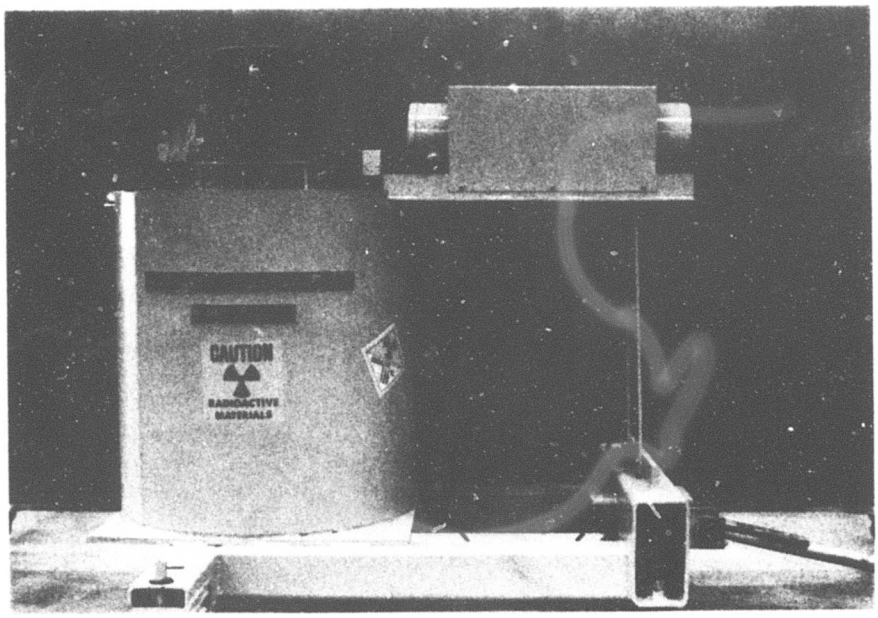


a. Side view TNC.

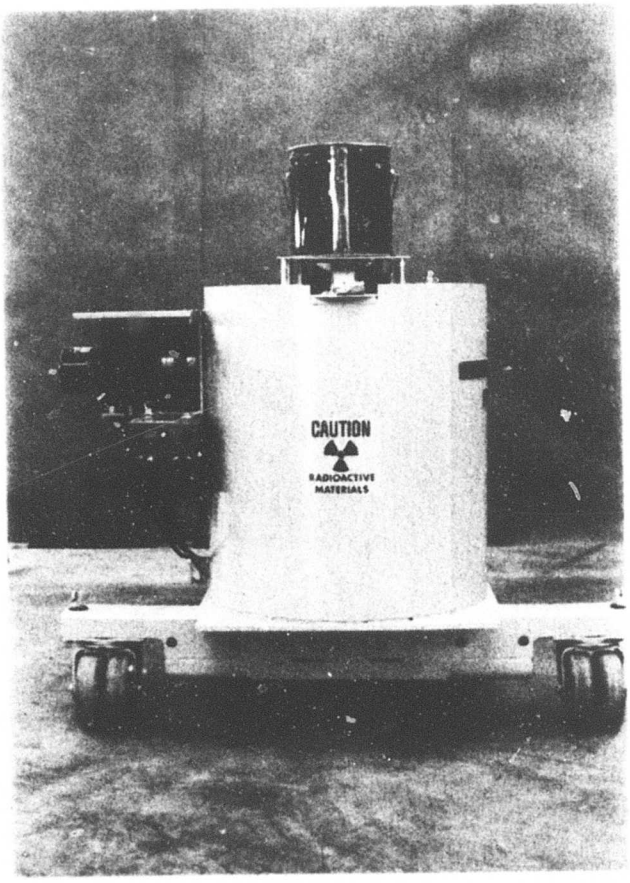


b. Front view TNC.

Figure 1. Thermal neutron cell (TNC).

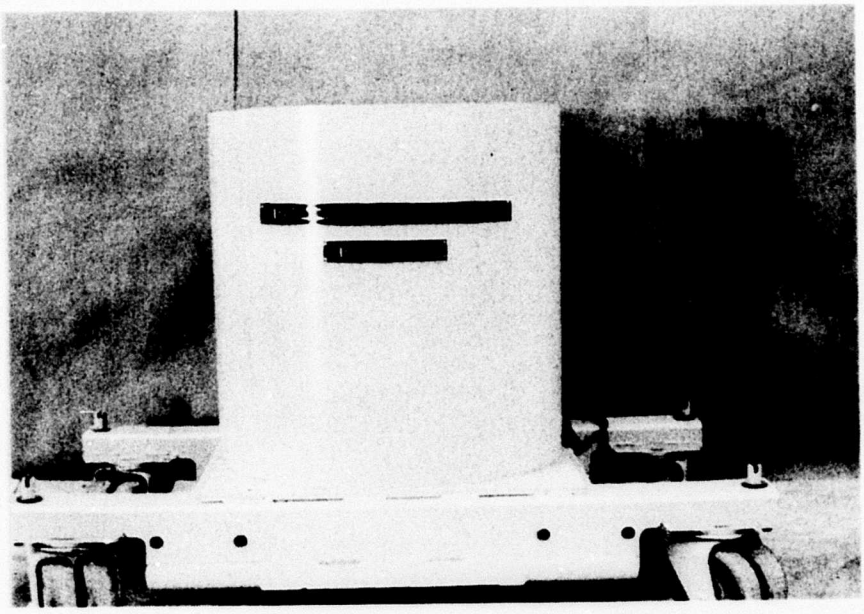


a. Side view FNC.

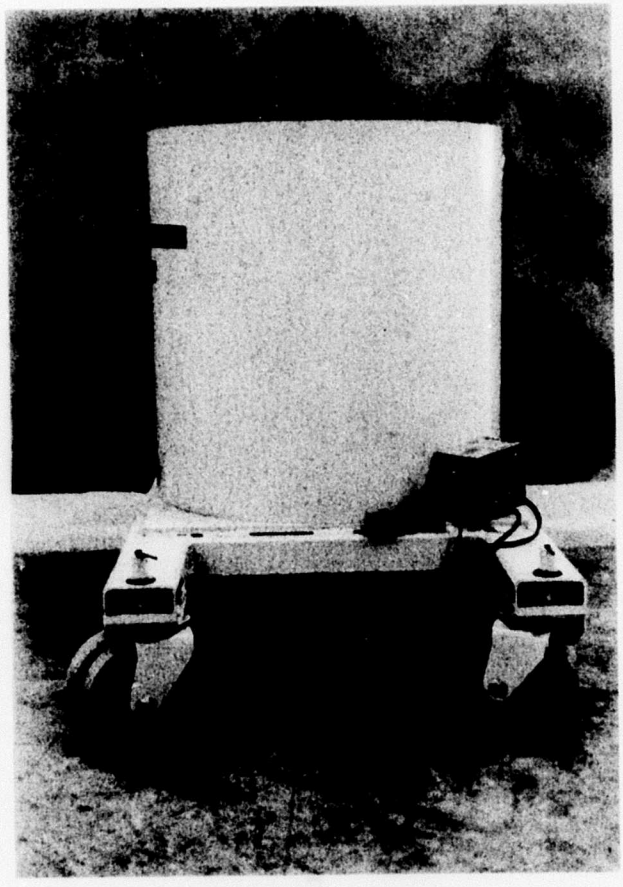


b. Front view FNC.

Figure 2. Fast neutron cell (FNC).

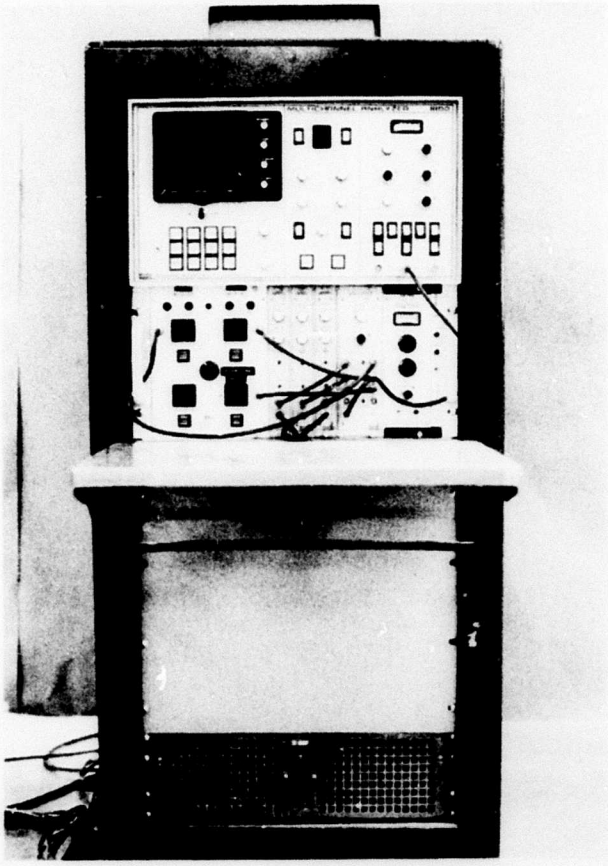


a. ACC - front view.

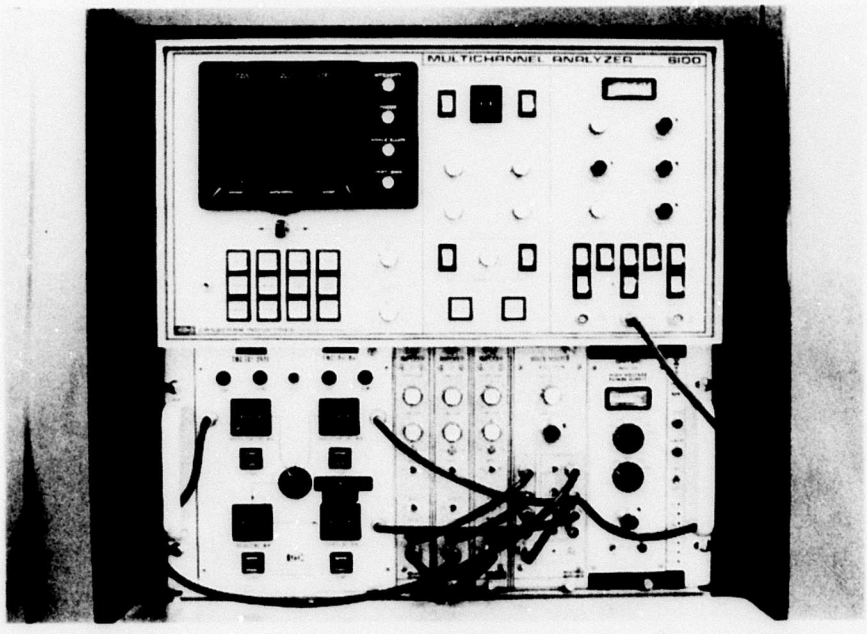


b. ACC - side view.

Figure 3. Activation counting cell (ACC).



a. Control unit.



b. Control unit - close up.

Figure 4. Control unit.

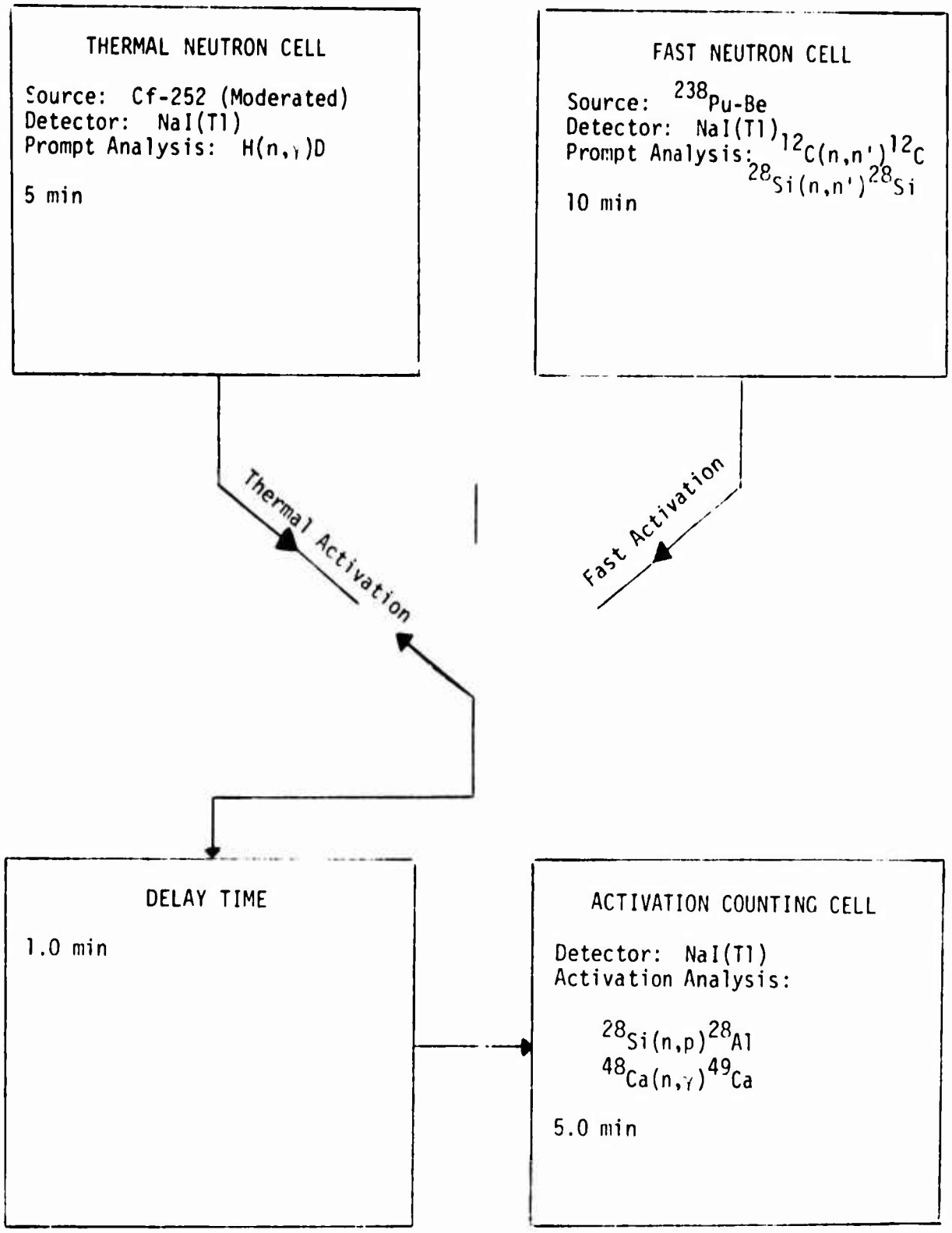


Figure 5. Analysis procedure flow diagram.

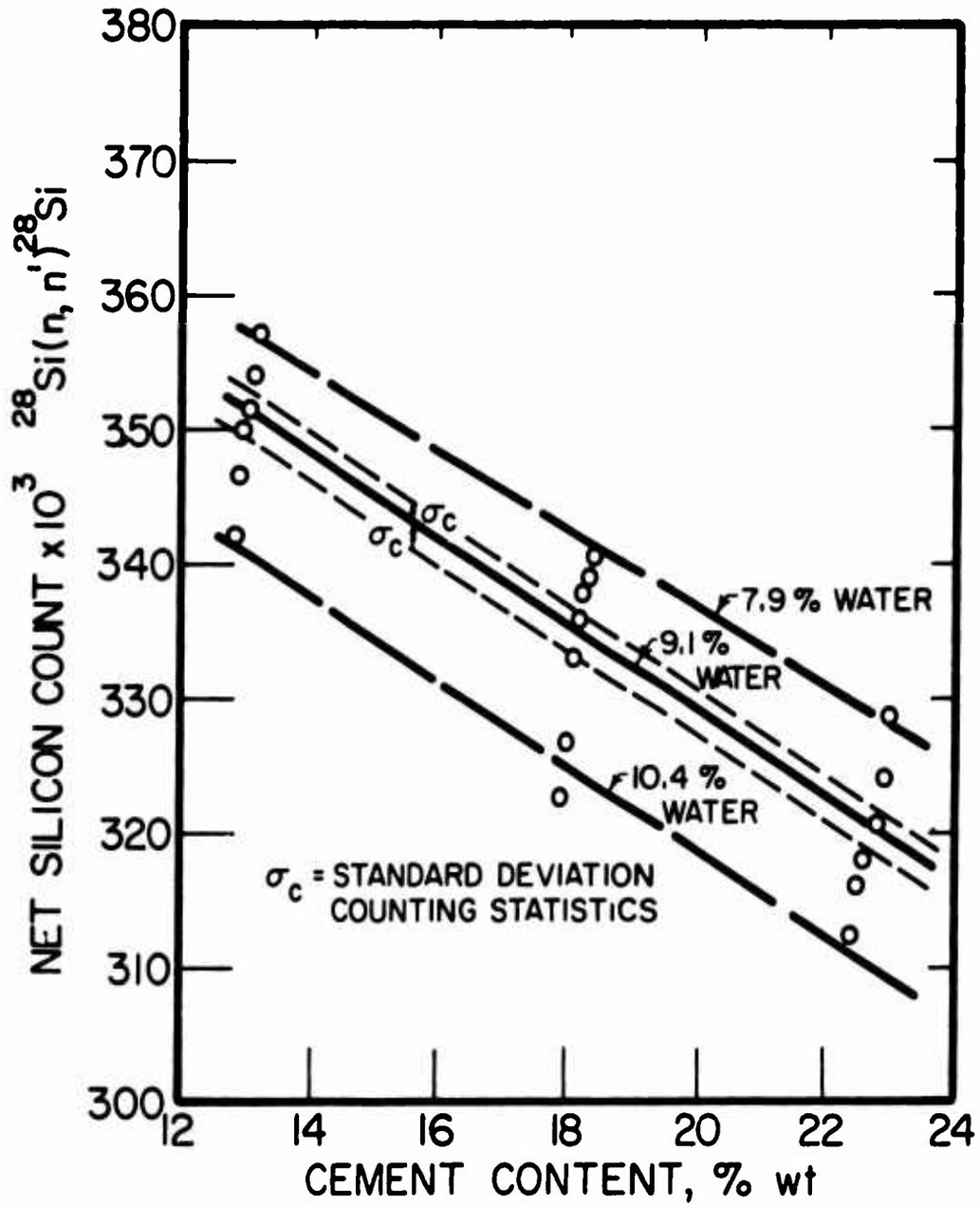


Figure 6. Cement content vs. silicon signature-ottawa sand (influence of water content on Si signature).

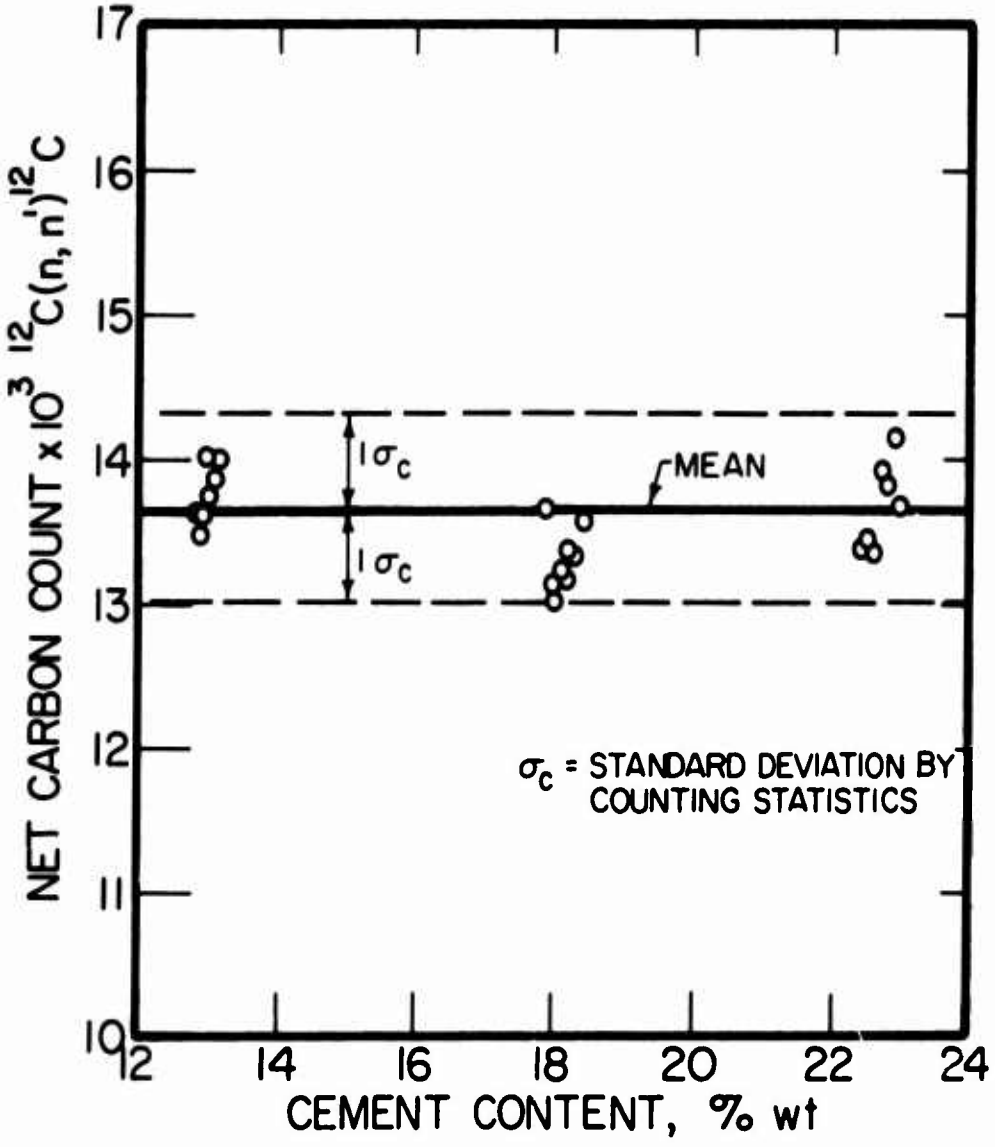


Figure 7. Cement content vs. carbon signature (FNC) ottawa sand (influence of water content on C signature).

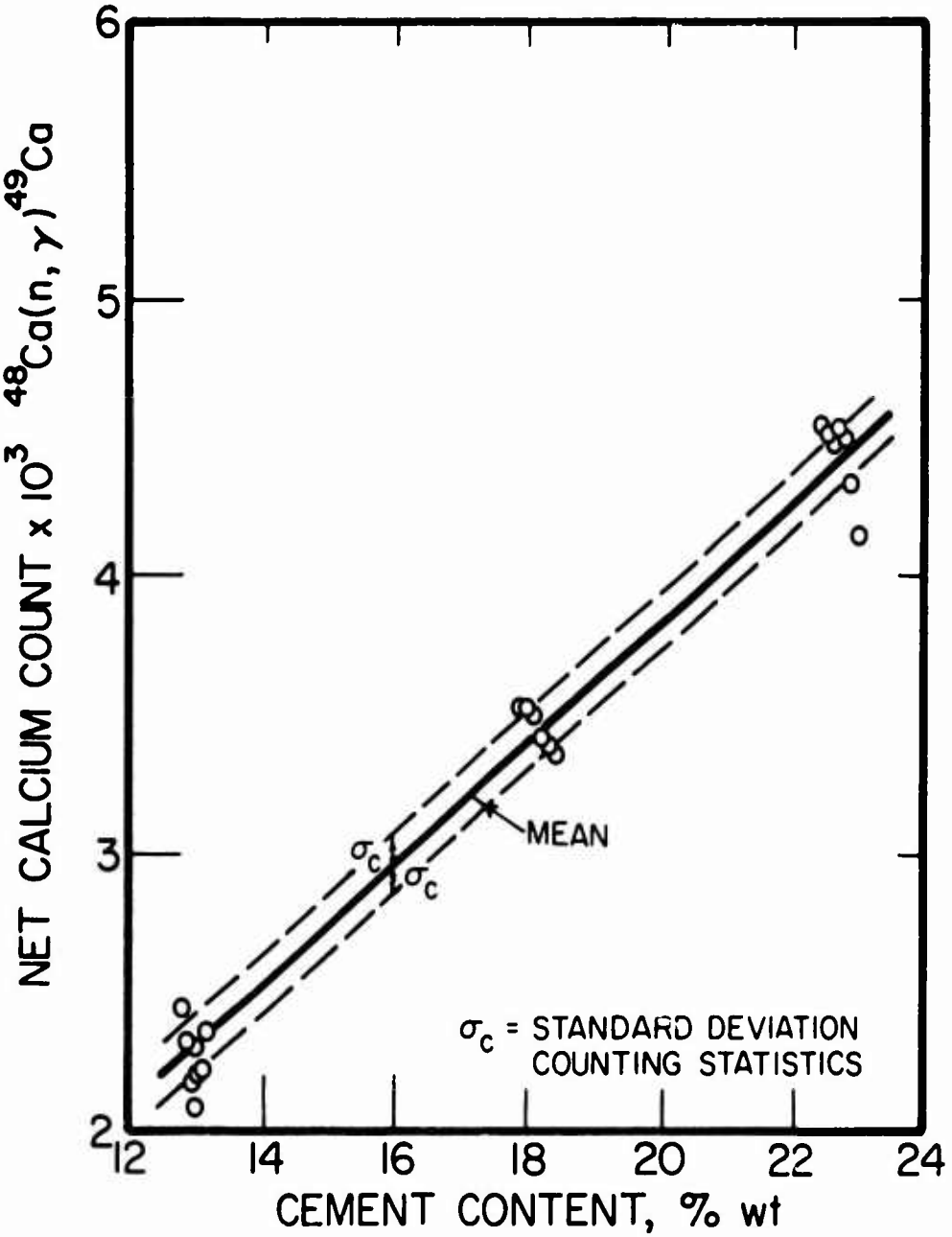


Figure 8. Cement content vs. calcium signature ottawa sand (influence of water content on Ca signature) [activation counting cell].

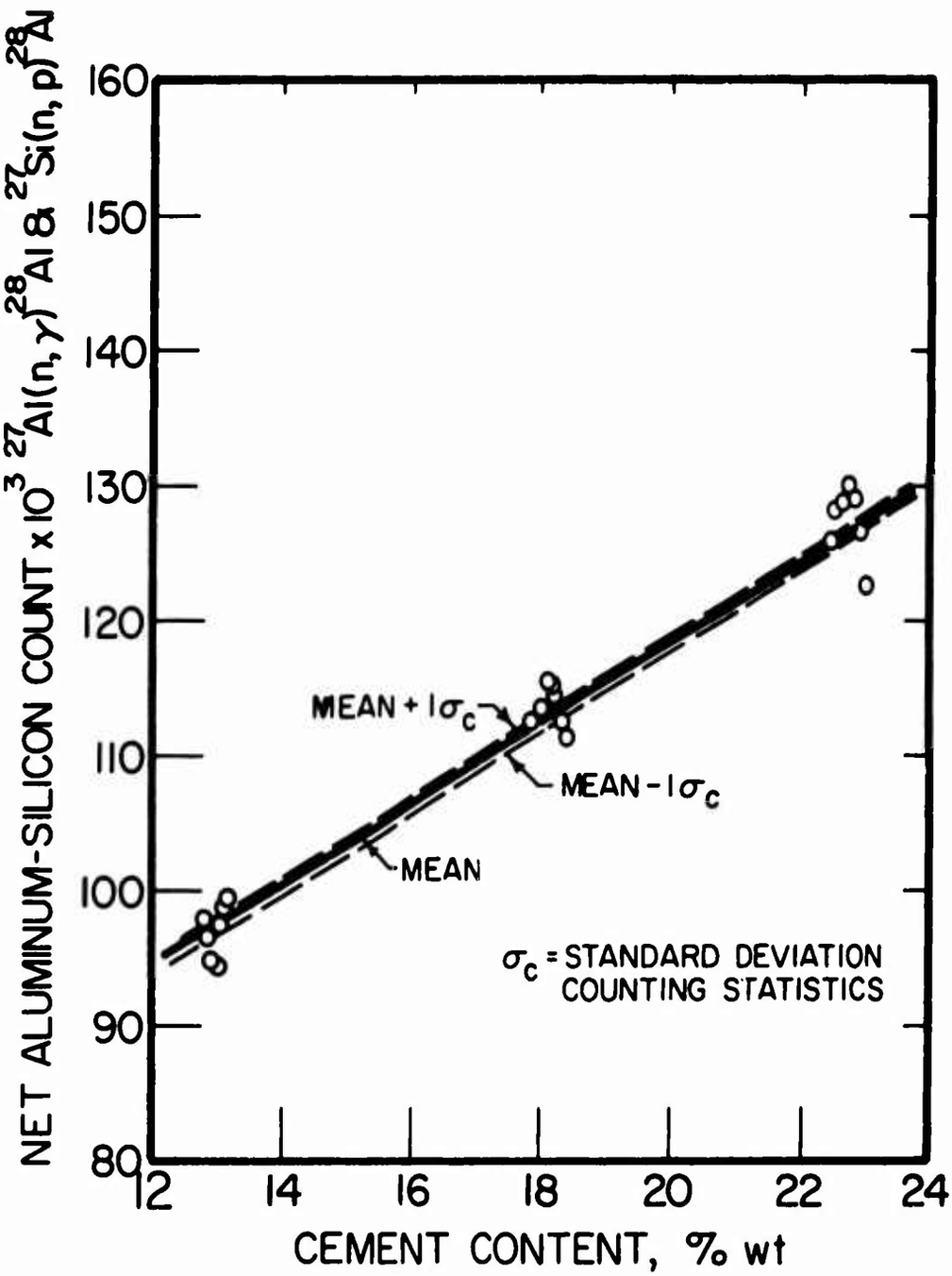


Figure 9. Cement content vs. aluminum-silicon signature ottawa sand (influence of water content on Al-Si signature) [activation counting cell].

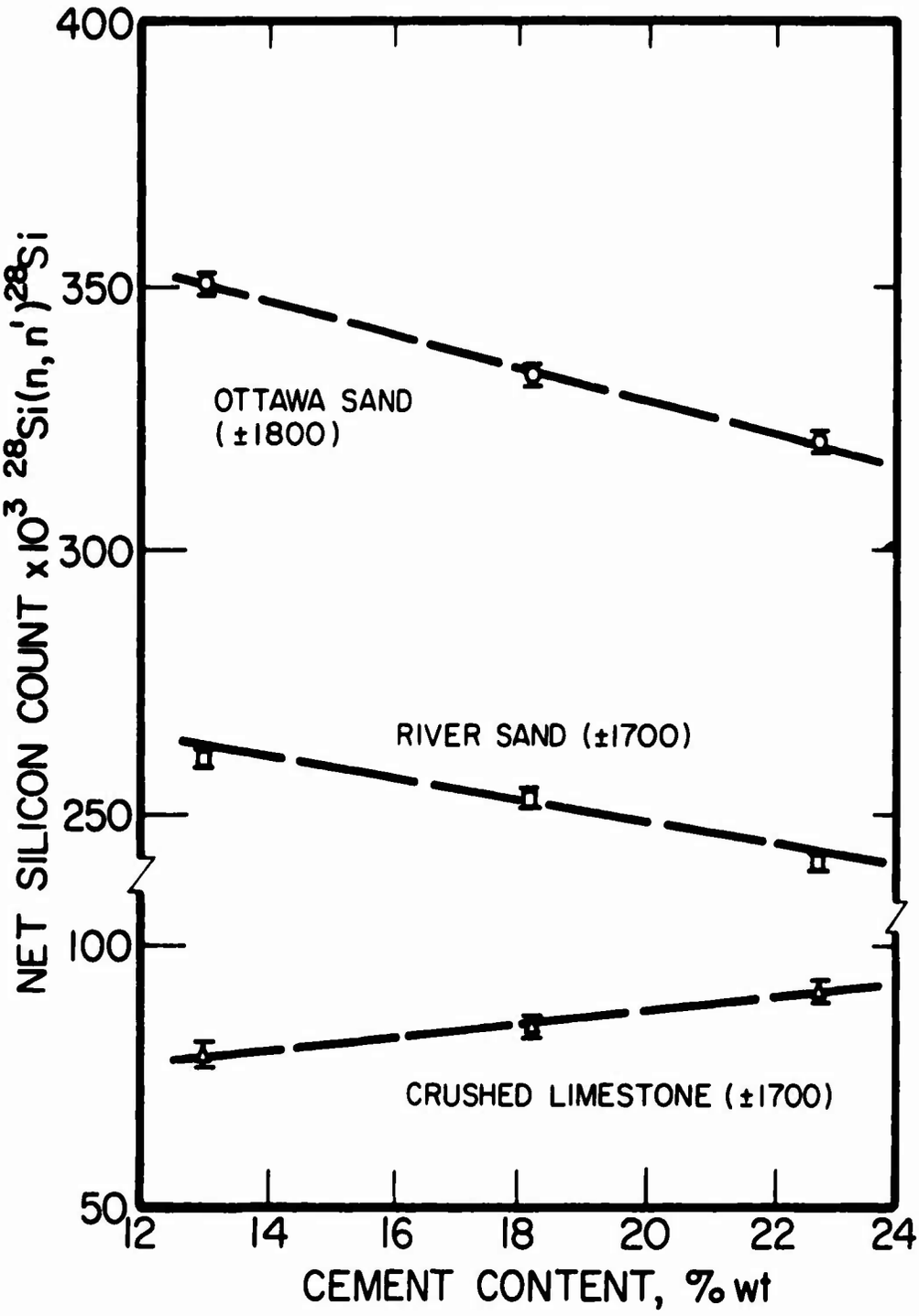


Figure 10. Cement content vs. silicon signature (FNC).

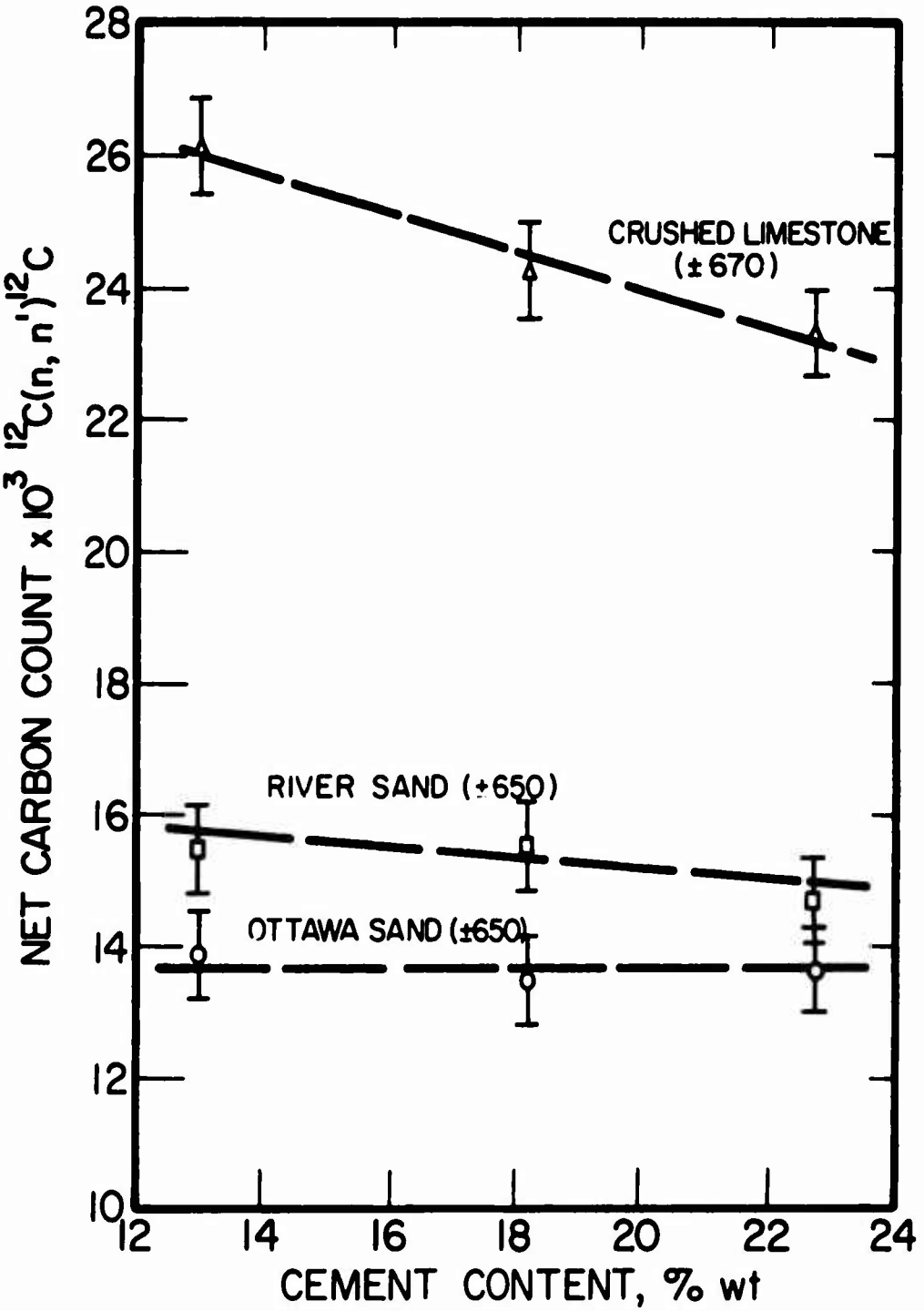


Figure 11. Cement content vs. carbon signature (FNC).

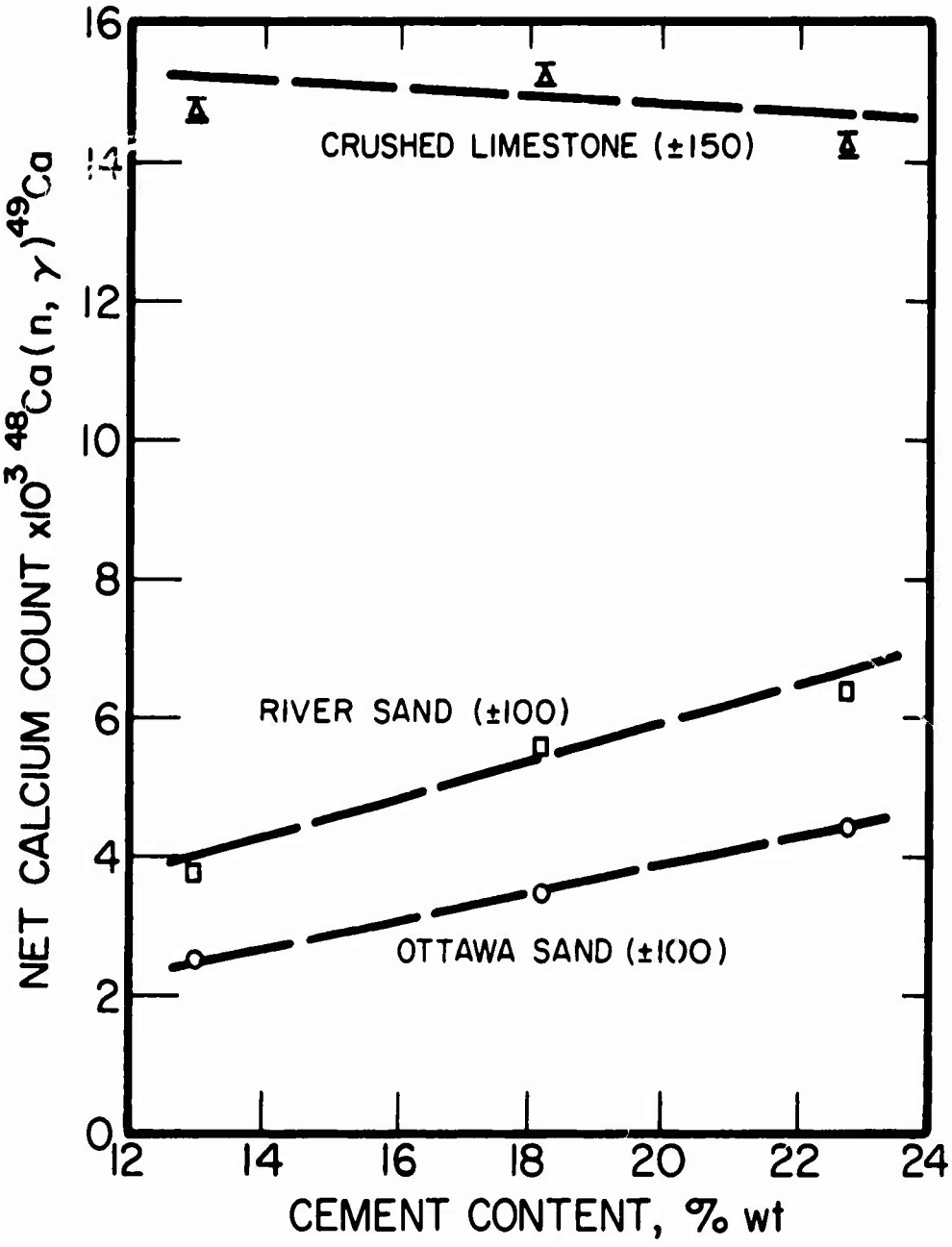


Figure 12. Cement content vs. calcium signature (activation counting cell).

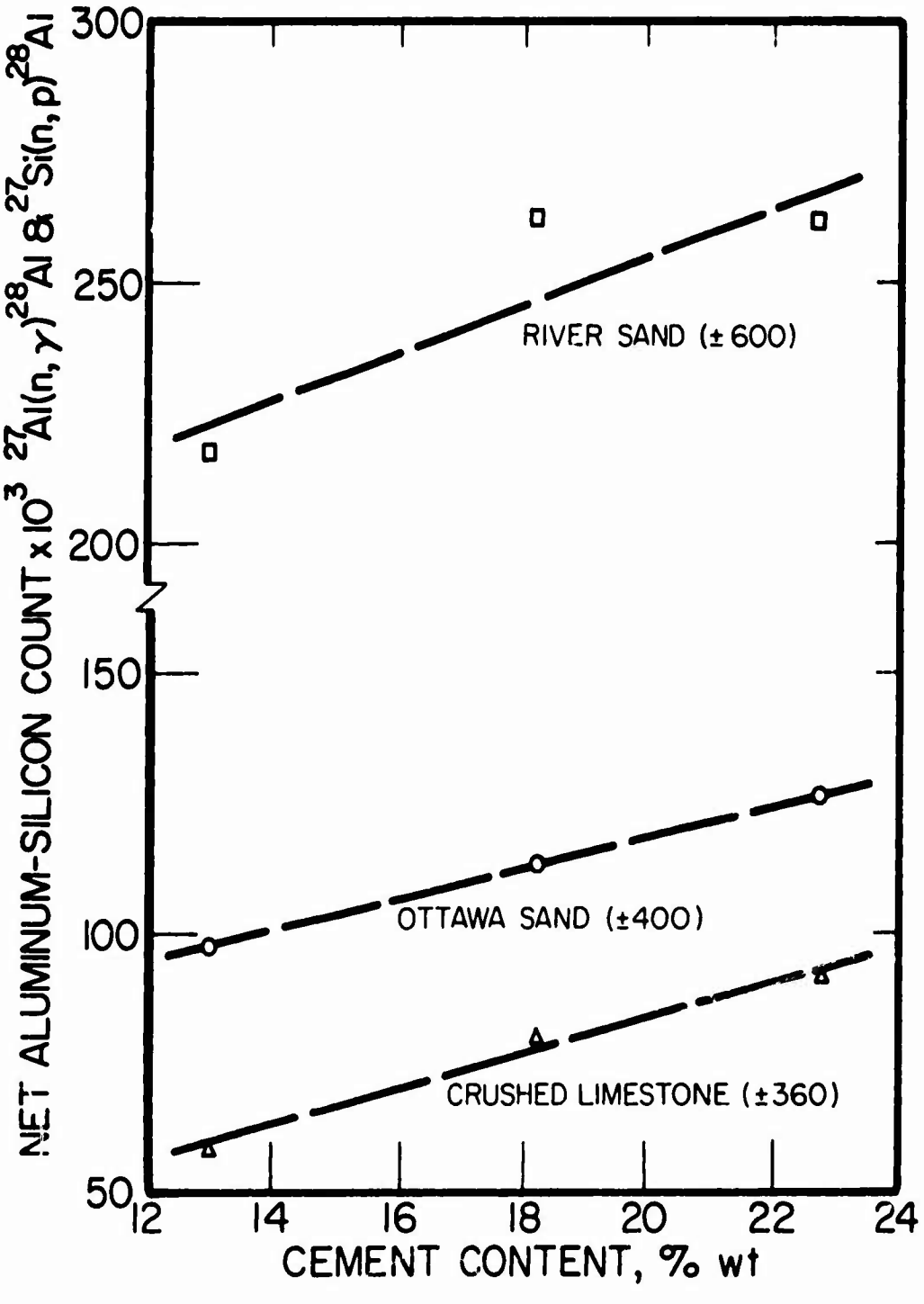


Figure 13. Cement content vs. aluminum-silicon signature (activation counting cell).

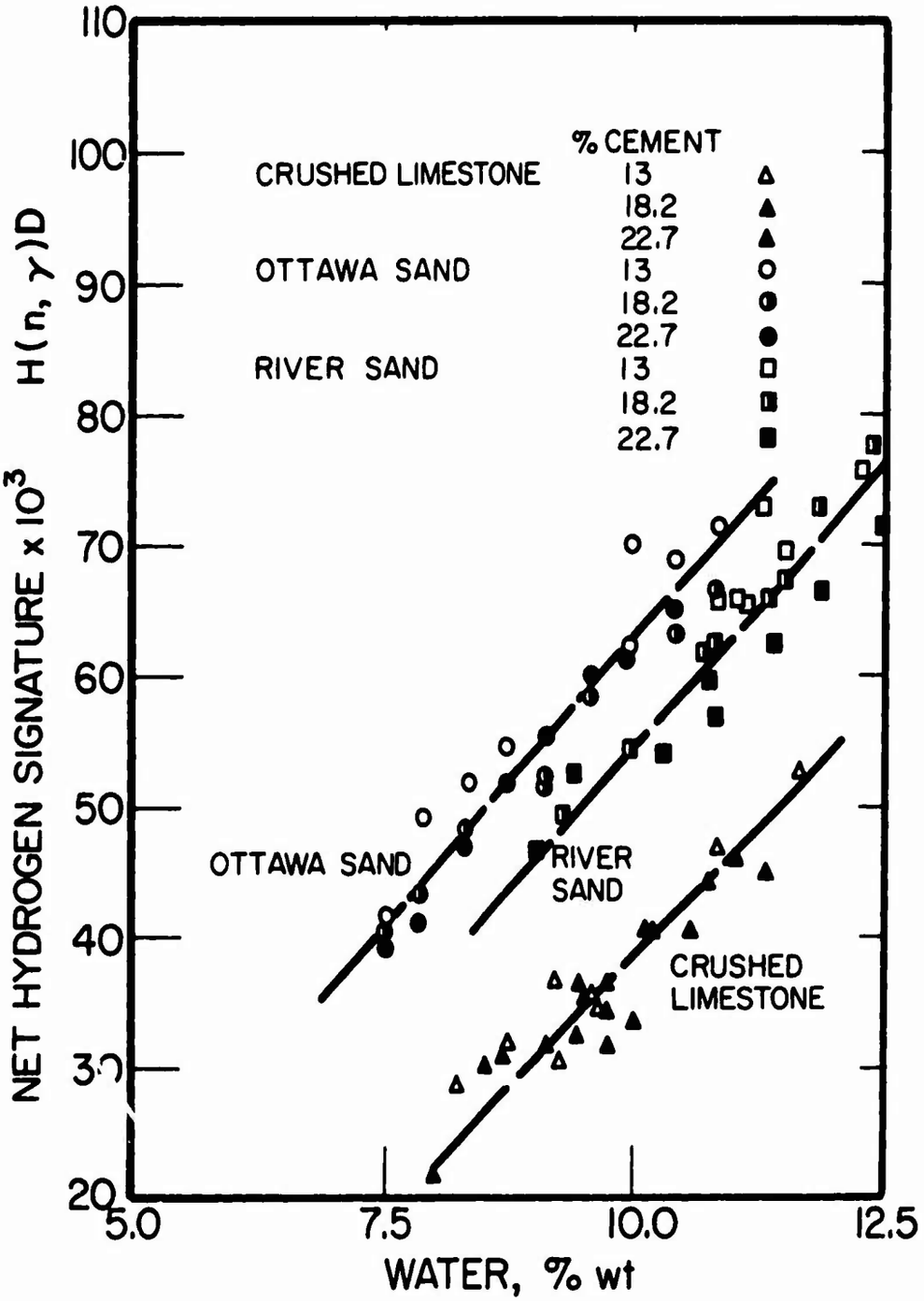


Figure 14. Water content vs. hydrogen signature (TNC).